ANL-77-65
Part III

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RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January—December 1977

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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RADIOLOGICAL AND ENVIRONMENTAL RESEARCH DIVISION ANNUAL REPORT

Ecology

January through December 1977

R. E. Rowland, Division Director
D. N. Edgington, Section Head

Preceding Report: ANL-76-88, Part III, January-December 1976

FOREWORD

The ongoing programs of the Ecological Sciences Section continued to be supported at the same level of effort in 1977 as in 1976. During the year two new programs were initiated: one to study the role of physical processes involved in transferring pollutants from the combustion of fossil fuels to the water surface, from the water to the sediments, and redistribution of sediment to the ultimate sink; the other to study the biogeochemical behavior of transuranic elements from the Windscale reprocessing plant. The latter program is being carried out with the valuable cooperation of the Fisheries Radiobiological Laboratory of the United Kingdom Ministry of Agriculture, Food, and Fisheries at Lowestoft.

In order to facilitate the changing research programs of the section in the Great Lakes, careful consideration was given as to whether we should acquire a larger research vessel. After much deliberation it was decided to have a new 58 ft fast work boat constructed. This vessel should be completed in time for the 1978 field season.

The field program initiated in 1976 to study the effects of atmospheric pollutants on the variability of midwestern cereal crops had a very successful first field season. The experiments showed that concentrations of SO_2 not much greater than ambient downwind of power plants had a marked effect on the yield of soybeans.

Studies of the effects of pollutants from power plants on aquatic organisms constitute a major part of the Great Lakes program. It has been shown that large thermal plumes attract the top predator fish, and studies are now underway to ascertain whether these fish, as a result of this attraction, accumulate more toxic materials because of their increased metabolic activity in the thermal water. Studies have continued on determining the possible effects of low concentrations of toxic materials, like cadmium, on phyto- and zooplankton. The use of zooplankton population and community responses to a pollutant appears to be a particularly useful technique.

The objective of the chemical studies in the lakes is to determine the concentrations of energy-related pollutants in the lakes and how they may change with time, and the mechanisms of transfer between compartments. Techniques have been developed to measure the concentrations of trace elements and to characterize chemical speciation.

Studies of the fallout radioactivity in the Great Lakes and elsewhere continue to provide an understanding of not only the behavior of these elements in the environment but also of major limnological and oceanographic processes. During 1977 techniques were developed to distinguish the oxidation states with widely differing chemical properties, in natural waters. This is important since chemical forms can affect biological availability and therefore transport to man.

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EFFECTS OF SO_2 ON CROP PLANTS: OVERVIEW

J. E. Miller

The "SO_2-Crop Plants Effects" program has undergone rapid growth in the past two years, and the project now has five full-time staff members. In this period, field and growth chamber approaches have been integrated to study the effects of SO_2 on soybeans. Field experimentation has taken precedence over growth chamber studies in the program, since economically significant effects of SO_2 on crops (yield reductions) can only be defined in field studies. Growth chamber studies are used primarily as a means of identifying important factors to be studied in the field, although the chamber experiments will also be useful in quantifying environmental interactions with SO_2 effects, which cannot be controlled in field experiments.

In 1977 a suitable site for the field experimentation was located on a private farm in Kendall County, Illinois (25 miles southwest of Argonne). Ten acres of soybean field were acquired and experimental plots were exposed to controlled levels of SO_2 by an open air release technique. Within the field plots, studies relating to the effects of SO_2 on the morphology, development, physiology, susceptibility to pathogens, and yield of soybeans are being conducted. A graduate student is also preparing a dissertation on SO_2-acid precipitation interactions at the field site. In addition, the site is utilized by the Atmospheric Physics Section to study the fluxes of air pollutants to crop canopies; this aspect will form an integral portion of the work on SO_2 effects. The following papers summarize the important findings during the 1977 field season.

AN OPEN AIR FUMIGATION SYSTEM FOR THE STUDY OF SULFUR DIOXIDE EFFECTS ON CROP PLANTS

J. E. Miller, R. N. Muller, D. G. Sprugel, H. J. Smith, and P. B. Xerikos

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To assess the potential for air pollutant damage to agronomic species properly, it is necessary that the experimental system satisfy several criteria. (1) The plants should be grown under agronomically "typical" conditions and the fumigation system should minimally disturb the microenvironment of the plants. (2) The fumigation system should be large enough to expose a sufficient number of plants to determine yield effects accurately. (3) The air pollutant should be delivered to the plants in a manner that is environmentally realistic for the pollutant in question. (4) The fumigation system should allow a reasonable amount of control of the mean exposure concentrations. To satisfy these criteria an "open air fumigation system" was designed for use in the SO_2-crop effects program and was utilized for the 1977 growing season on soybeans. The system is similar to the Zonal Air Pollution System used by the Corvallis Environmental Research Laboratory in studies of SO_2 effects on a range ecosystem.[1]

In essence, the open air fumigation system consists of arrays of pipes suspended over the surface of the crop, through which diluted SO_2 is released at controlled rates. The 1977 experiments, which were conducted in an "agronomically typical" field of Wells soybeans in Kendall County, Illinois, used four pipe arrays (fumigation units), as illustrated in Figure 1. Each individual fumigation unit consisted of five 96-ft sections of 1-in aluminum pipe (release lines) extending at approximately 20-ft intervals from an 80-ft baseline pipe. The SO_2 air mixture was released through 1/32-in, horizontally oriented holes in the release lines at 2-1/2-in intervals. The release lines and baseline were attached to metal fenceposts and suspended approximately 1 ft over the crop canopy so that the pipes could be raised as the canopy increased in height. Air flow from the SO_2 delivery sheds (Figure 1) to the fumigation units was accomplished by compressors, and the SO_2 was bled at controlled rates into

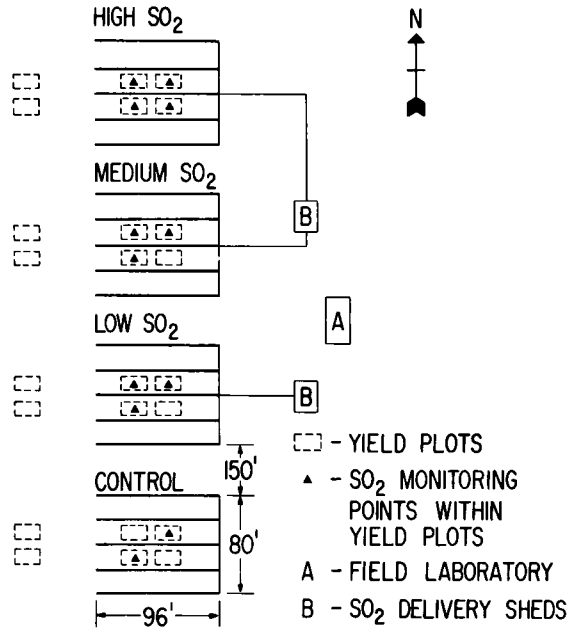
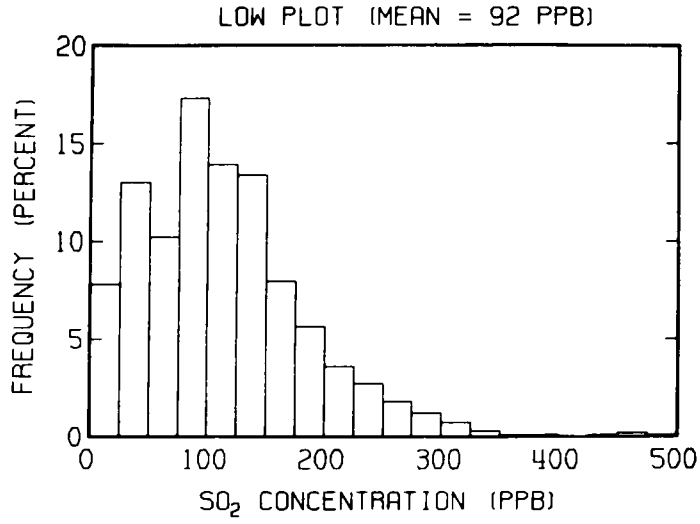


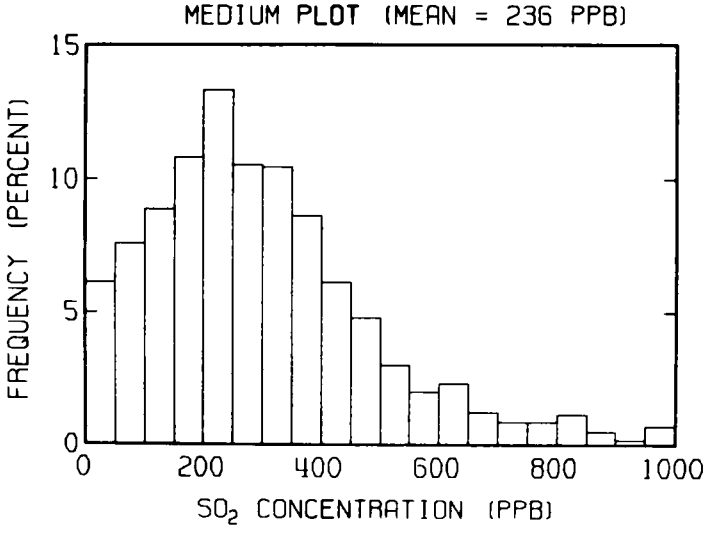
FIG. 1.--Diagrammatic illustration field fumigation system at Kendall County field site (1977). (ANL Neg. 149-78-59)

the pipes immediately downstream from the compressor to give the desired concentrations of SO_2 in the plots.

The SO_2 concentrations in the four plots were measured at the locations indicated in Figure 1. To accomplish this, air was continually pumped from each of the monitoring points through polyethylene sampling lines to SO_2 monitors in the field trailer. The flow in each of the sampling lines was automatically diverted to an SO_2 monitor for 2 min every 16 min and the measured concentrations were recorded.

In the 1977 experiment the three treated plots of soybeans were fumigated on 24 days from 13 July to 29 August for an average of 4 hr 44 min a day. Fumigations were attempted only when the wind direction was predominantly northerly or southerly so that the SO_2 was carried across the plots. The geometric mean treatment concentrations at the monitoring locations for the three treated plots during the fumigation periods were 92, 236, and 706 ppb of SO_2 and are designated the low, medium, and high plots, respectively. However, the fumigation regimes for each treatment plot are better expressed as frequency distributions (Figure 2), since constantly fluctuating wind speeds and turbulence cause substantial deviations around the mean concentrations. A typical example of the fluctuations in SO_2 concentration with time is illustrated in Figure 3.





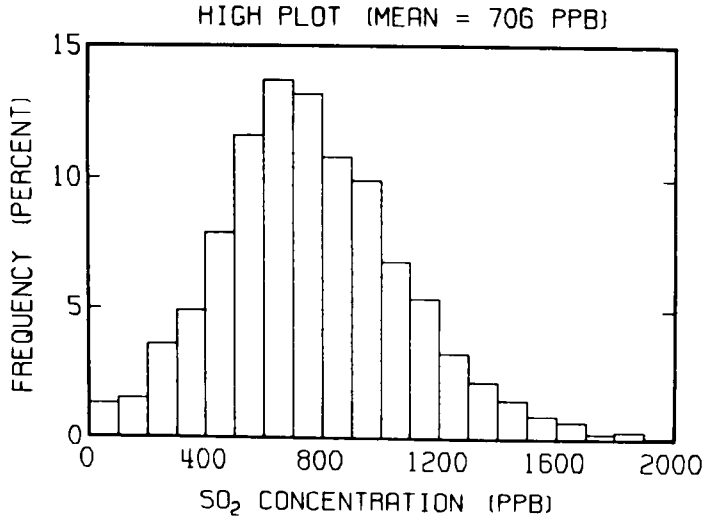


FIG. 2.--Frequency distributions of SO_2 exposure concentrations for field plots in 1977. (ANL Neg. 149-78-233)

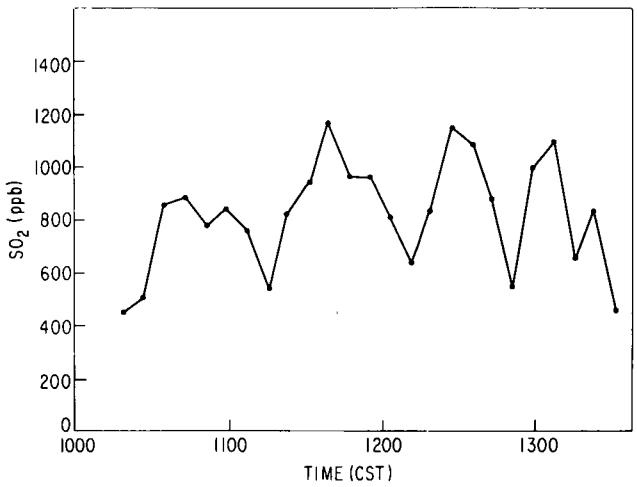


FIG. 3.--SO_2 concentrations in the high SO_2 plot during fumigation on 13 July 1977. (ANL Neg. 149-78-242)

This is similar to what occurs in an actual SO_2 pollution episode and is, therefore, preferable to the usual experimental techniques in which plants are exposed to steady concentrations.

Spatial differences were observed in SO_2 concentrations within the treatment plots, as would be expected since the SO_2 release lines actually constitute a series of point sources in close proximity. The SO_2 concentrations at four equally spaced points between two of the pipes in the high treatment plot were monitored for three fumigations. The normalized concentration gradient averaged 1.00, 0.77, 0.75, and 0.66 from the upwind side. The yield subplots were located in that relatively uniform central region between the pipes (Figure 1), since only rather small SO_2 concentration gradients were apparent in that area. Each subplot consisted of four 20-ft rows with a buffer row between it and the release pipes. Differences in the mean SO_2 concentrations between the individual monitoring locations in each of the treatment plots were also noted; however, these variations were small enough to be considered insignificant for most purposes (± 7% of the overall plot mean).

Experience with the open air fumigation system during the 1977 field season has verified its usefulness as a tool in studies of sulfur dioxide effects on field crops. The temporal variations in pollutant gas concentrations obtained with this technique are advantageous when studying pollutants originating primarily from point sources, since the fluctuation simulates actual conditions. The problems with spatial variation in exposure concentrations can be overcome

by careful selection for the areas of maximum uniformity within the system.

Reference

1. J. J. Lee and R. A. Lewis, Field experimental component: the bioenvironmental effects of sulfur dioxide, The Bioenvironmental Impact of a Coal-Fired Power Plant, R. A. Lewis and A. S. Lefohn, Eds., First Interim Report, EPA-600/3-76-002 (1976).

EFFECT OF SULFUR DIOXIDE FUMIGATION ON DEVELOPMENT AND YIELD OF FIELD-GROWN SOYBEANS

D. G. Sprugel, J. E. Miller, R. N. Muller, H. J. Smith, and P. B. Xerikos

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One of the primary goals of the SO_2 fumigation study is to determine the effect of sulfur dioxide exposure on soybean yield at harvest. It is nearly impossible to grow soybeans to normal harvest maturity in a growth chamber or greenhouse, and ultimate yield reduction cannot be predicted from immediate physiological or pathological effects. Thus, it is not possible to estimate economic consequences of different SO_2 pollution levels without field experimentation.

In order to predict the effects of the SO_2 treatments on yield in the open-air fumigation study, four sample plots were established near the center of each fumigation plot.[1] Each plot was 20 ft long by four rows wide, and each row was harvested and weighed separately. Since preliminary monitoring had shown that SO_2 levels near the distribution pipes were considerably more variable and often much higher than those elsewhere in the fumigation plot, the harvest plots were centered between the pipes and excluded crop rows directly under or adjacent to the pipes. In addition, to determine the effect of variation in soil fertility across the field, two "plot control" sampling areas were established 40 to 50 feet west (upwind) of each fumigation plot and designated as the "high-control," "medium-control," "low-control," and "control-control" plots.

Analysis of the yield data showed that there were significant and rather large yield differences among the "plot controls," suggesting considerable variation in the soils across the study field (Table 1, column 2). Soil samples collected in October reflected this variation; in particular, the control-control plot had significantly more organic matter and a higher cation exchange capacity than the other control plots. It is thus inappropriate to compare the fumigated plots with each other directly. However, there were no yield or soil differences between the control plot with distribution pipes but no SO_2 and the pipeless

Table 1. Variation in bean yield, chaff weight, and harvest ratio among plots subjected to different SO_2 concentrations by the OAFS system. Values are means ± S.E.

Plot	Fumigated	Control	Difference, %
Bean Yield, (kg/ha)			
High	1636 ± 52	2992 ± 120	-45 (p <.001)
Medium	2482 ± 65	3140 ± 48	-20 (p <.001)
Low	3052 ± 92	3478 ± 101	-12 (p <.01)
Control	2566 ± 77	2557 ± 73	0
Chaff Weight, (kg/ha)			
High	1817 ± 42	2394 ± 88	-24 (p <.001)
Medium	2211 ± 41	2390 ± 36	-7.5 (p <.05)
Low	2422 ± 60	2485 ± 66	-2.5 (n.s.)
Control	2246 ± 89	2187 ± 76	+2.7 (n.s.)
Harvest Ratio, (kg beans/kg chaff)			
High	0.90 ± .04	1.25 ± .07	-28 (p <.001)
Medium	1.12 ± .04	1.31 ± .03	-15 (p <.01)
Low	1.26 ± .05	1.40 ± .06	-10 (n.s.)
Control	1.14 ± .06	1.17 ± .05	-2.3 (n.s.)

control-control plot, which indicates that the presence of the pipes and the disturbance involved in installing the system did not affect yield to a significant degree. Thus the yield reductions due to fumigation were estimated by comparing each plot to its own control.

As shown in Table 1, soybean yield in the high-SO_2 plot (geometric mean = 706 ppb) was reduced 45% ($p < 0.001$) compared to the high-control plot. This large yield reduction was not unexpected, as considerable tissue damage was observed in soybeans on this plot during the summer. In the medium-SO_2 plot (g.m. = 236 ppb) yield was reduced by 20% ($p < 0.001$). Although temporary reductions in photosynthesis were observed in these plots during the fumigations,[2] visible injury was never observed in the yield plots under this treatment. Minor necrosis was, however, observed in the rows

under and adjacent to the SO_2 delivery pipes, suggesting that the SO_2 levels in the yield plots may have been close to those required to cause visible injury. In the low-SO_2 plot (g.m. = 92 ppb) yield was apparently reduced 12% by the fumigation ($p < 0.01$). This result was quite unexpected since neither tissue damage nor significant photosynthetic reduction was ever observed on this plot. Further study will be needed to determine whether this apparent yield reduction was actually due to SO_2 effects or simply to soil differences between the low and low-control plots, although the October soil samples showed no significant differences between these plots.

In addition to the reductions in bean yield, there were differences in chaff weight (stems and pods) between the fumigated and control plots (Table 1). However, the chaff weight differences were smaller than the yield differences, and were not statistically significant in the low plot. Thus the harvest ratio (bean yield/chaff weight) was significantly reduced in the high and medium SO_2 plots, showing that the SO_2 treatment had its greatest effect on the economically important part of the plant.

To provide more detailed data on the nature of the SO_2 effects, ten typical plants were selected from each of the treated and control plots at the time of harvest, separated into stems, pods, and seeds and weighed individually. Results for the high and high-control plots are shown in Table 2. These data show that the yield decrease in the high plot was due both to a decrease in the total number of seeds per plant and a decrease in the mean weight per seed. The number of pods per plant was reduced, but the number of seeds per pod was not affected. However, a much higher fraction of the seeds were unfilled in the treated plot. The reduction in chaff weight resulted from decreases in both pod weight and stem weight. Mean plant height was not affected by the treatment.

The equivalent data from the medium plots showed the same trends but the differences were smaller and none was significant at this sample size. However, more detailed sampling from the general harvest showed that mean seed weight was significantly reduced in both the medium and low plots compared to their respective controls (Table 3).

Table 2. Variation in some morphological parameters of field-grown plants exposed to high SO_2 levels. Values are means ± S.E.

	High plot	Control	Change, %
Length, cm	115.3 ± 2.1	117.2 ± 1.5	-2.1 (n.s.)
No. of nodes	15.7 ± 0.2	16.3 ± 0.3	-4.0 (n.s.)
Stem weight, g	8.3 ± 0.2	10.0 ± 0.4	-17 ($p < 0.001$)
No. of pods	39.6 ± 1.3	46.4 ± 1.6	-15 ($p < 0.01$)
Weight of pods, g	4.03 ± 0.16	5.18 ± 0.17	-22 ($p < 0.001$)
No. of filled seeds	97.2 ± 3.3	119.9 ± 3.8	-19 ($p < 0.001$)
Unfilled seeds	13.3 ± 1.0	7.9 ± 1.1	-67 ($p < 0.01$)
Total seeds/pod	2.79 ± 0.01	2.76 ± 0.02	+1.3 (n.s.)
Mean seed weight[a], g	0.139 ± 0.003	0.175 ± 0.003	-20 ($p < 0.001$)
Total seed weight, g	13.7 ± 0.7	20.9 ± 0.6	-35 ($p < 0.001$)

[a]Filled seeds only.

Table 3. Variation in mean bean weight and protein content among field plots subjected to different SO_2 concentrations. Values are mean ± S.E.

Plot	Fumigated	Control	Difference, %
Mean Bean Weight, g			
High	0.131 ± 0.002	0.161 ± 0.002	-19 ($p < 0.001$)
Medium	0.163 ± 0.001	0.175 ± 0.001	-6.7 ($p < 0.001$)
Low	0.163 ± 0.001	0.167 ± 0.001	-2.7 ($p < 0.05$)
Control	0.172 ± 0.001	0.171 ± 0.002	+0.6 (n.s.)
Bean Protein Content, %			
High	38.4 ± 0.2	39.6 ± 0.4	-2.8 ($p < 0.01$)
Medium	40.1 ± 0.2	40.8 ± 0.3	-1.5 (n.s.)
Low	40.5 ± 0.3	40.2 ± 0.3	+0.7 (n.s.)
Control	41.1 ± 0.3	40.9 ± 0.3	+0.5 (n.s.)

To examine the effect of the SO_2 treatment on bean quality, samples from each harvested row were analyzed for protein and oil content by the University of Illinois Department of Agronomy. Oil content of the beans averaged 21.4% and was apparently not affected by the SO_2 fumigation. However, protein content of the beans in the high SO_2 plot was reduced from 39.6% to 38.4% ($p < 0.01$, Table 3). A smaller, non-significant decrease in protein content was observed in the medium plot.

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1. J. E. Miller, R. N. Muller, D. G. Sprugel, H. J. Smith, and P. B. Xerikos, An open air fumigation system for the study of sulfur dioxide effects on crop plants, this report.
2. R. N. Muller, J. E. Miller, D. G. Sprugel, and H. J. Smith, Photosynthetic response of field-grown soybeans to fumigations with sulfur dioxide, this report.

PHOTOSYNTHETIC RESPONSE OF FIELD-GROWN SOYBEANS TO FUMIGATIONS WITH SULFUR DIOXIDE

R. N. Muller, J. E. Miller, D. G. Sprugel, and H. J. Smith

Assessment of the potential economic impact of air pollutants on crops requires a thorough understanding of the physiological response of crop species to the pollutants in question. Some of the most important responses are those affecting photosynthesis. The field fumigation system[1] permits studies of photosynthetic response during and after a fumigation. This report describes studies designed to assess these responses in soybeans subjected to a range of fumigation concentrations of SO_2.

Photosynthesis was measured by a ^{14}C assimilation technique[2] which allows multiple samples with little modification of the leaf microenvironment. Briefly, a portion of leaf tissue is exposed to an atmospheric mixture containing a known quantity of $^{14}CO_2$ through a hand-held clamp. The exposed tissue is then excised and processed for scintillation counting. The rapid fixation of the tissue after exposure precludes photorespiratory loss of the fixed ^{14}C, and hence, the values of ^{14}C fixation obtained may be related to gross photosynthesis (GP). Light intensity and stomatal diffusive resistance were routinely measured with each photosynthetic measurement.

Experiments were conducted throughout the summer of 1977 to follow photosynthesis in the control and treatment plots during the course of individual fumigations. The largest and most consistent response to the treatments was observed in the high SO_2 plot. In a study made on the first day of fumigation (July 13), light intensities remained well above saturation levels (Figure 1) and ambient temperatures ranged from 27 to 33°C. The geometric mean SO_2 concentration for the fumigation period was 769 ppb. GP continued at prefumigation rates for at least 15 min after initiation of the fumigation. The initial response, observed 45 min after initiation of fumigation,was a depression of GP to 42% of the control rate. During the rest of the fumigation GP remained depressed to 37 to 57% of the control rate (Figure 1). During the 1-1/2-hr period following the fumigation there was little apparent recovery of GP relative to control plants;

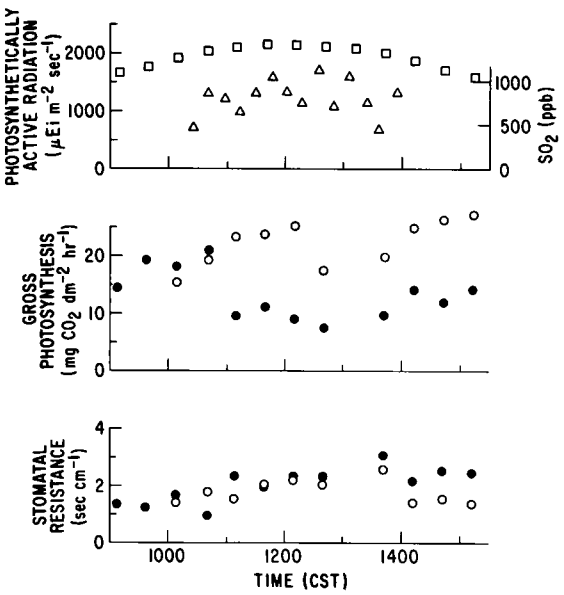

FIG. 1.--Photosynthetic rate and stomatal resistance of plants in the high SO_2 plot (●) and control area (O) on the first day of fumigation. Confidence intervals are 1 standard error. Upper graph shows photosynthetically active radiation (□) and SO_2 concentration (△).

however, the absolute rates did increase from a mean value of 9.6 mg CO_2/dm^2/hr during the fumigation to 13.5 mg CO_2/dm^2/hr at the end of the fumigation period ($p < 0.01$). Stomatal diffusive resistance on this day showed no significant response until 3 hr after initiation of the fumigation, after which resistance increased 19 to 71%. There was no correlation between stomatal resistance and photosynthetic response of the plants. Visible injury of leaf tissue was observed throughout the summer in the high SO_2 plot, in which SO_2 concentrations ranged from 0 to 2600 ppb.

In studies in the medium plot on August 12, there was no change in photosynthesis for over 3 hr following the initiation of fumigation. At this time GP in the medium plot was reduced by 17 to 33% at average fumigation concentrations of 136 to 405 ppb. Apparent recovery of GP was observed 1 to 2 hr after the end of fumigation. As observed previously, no correlation was observed between photosynthetic response and stomatal resistance. As the summer progressed, plants in the medium SO_2 plot exhibited an apparent decrease in sensitivity to fumigations of comparable magnitude and duration. Visible injury of the leaf tissue was never observed in the medium plot. The photosynthetic depression observed under the fumigation conditions of the medium plot and lack of visible injury in those plants indicates that a physiological response

independent of tissue injury occurs, which may significantly influence yield of plants exposed to lower concentrations of SO_2.

A comparison of photosynthetic response to the three fumigation regimes was made on July 20 (Figure 2). Gross photosynthesis was measured in the high plot two hours after fumigation had begun followed by measurements in the medium and low plots. During the period of study (12:56–14:22) light values remained well above the saturation point (1500 $\mu Ei/m^2/sec$). The arithmetic mean SO_2 concentrations in the three plots from the beginning of the fumigation until the middle of the respective photosynthetic measurements were 94, 191, and 590 ppb, respectively. In the high and medium plots GP was reduced to 53% and 63% of their respective control values ($p < 0.01$). In the low plot GP was apparently reduced by 10%; however, this difference was not statistically significant. Stomatal diffusive resistance was increased (10 to 16%) in plants of all three treatments ($p < 0.01$). The relative magnitude of the increased resistance was not related to the degree of photosynthetic depression in the same plants.

The observed photosynthetic response in the three plots throughout the summer was similar in magnitude to that observed on July 20. GP in the high plot was depressed to 37 to 63% of the control, and in the medium plot to

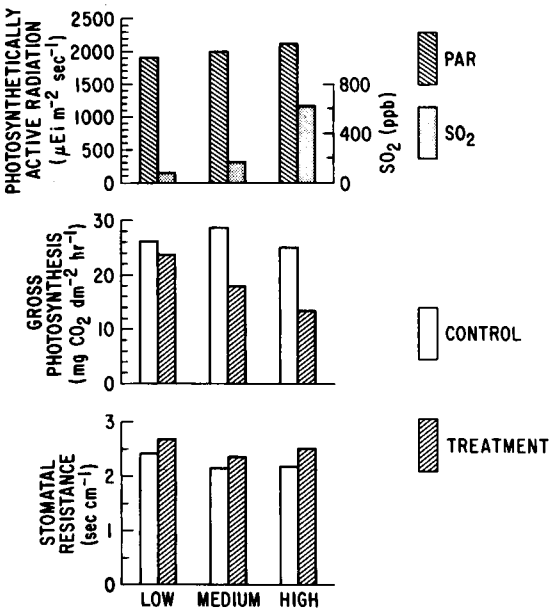

FIG. 2.--Comparison of photosynthetic rate and stomatal resistance of soybeans in the three treatment plots and control areas (July 20, 1977). Determinations were made within a total time period of 90 min. Upper graph shows photosynthetically active radiation and geometric mean SO_2 concentration from the beginning of the fumigation until the time of each measurement.

63 to 83%. In the low plot the gross photosynthetic response ranged from 90 to 137% of the control values. The 37% stimulation in the low plot, which occurred on a single occasion, was significant at the 0.01 level. Taken over the entire summer, photosynthetic response showed a curvilinear relationship to average SO_2 concentration (Figure 3). The data suggest a stimulation of GP at low concentrations under some conditions followed by reduction at increased concentration ($> \sim 100$ ppb).

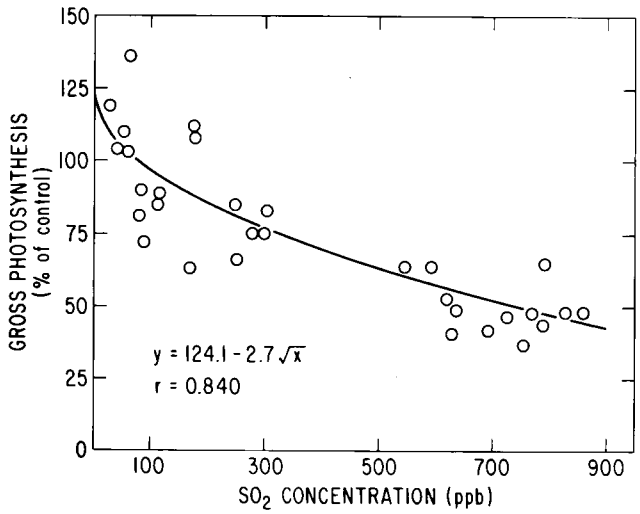

FIG. 3.--Relationship between photosynthetic response (as percent of the control) and SO_2 concentration (geometric mean value from the beginning of each fumigation to the time of each measurement).

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ELEMENTAL CONCENTRATION IN SOYBEANS FUMIGATED WITH SULFUR DIOXIDE

D. G. Sprugel, J. E. Miller, and R. N. Muller

One of the objectives of the soybean SO_2 study[1] was to determine the effect of SO_2 fumigation on the elemental content of soybean tissues and harvested soybeans. Samples of leaves, stems, and pods (including seeds) were collected from each "yield" plot on four dates during the summer and analyzed for N, S, P, K, Ca, Mg, Cu, Zn, and Mn by the Soil and Plant Analysis Laboratory in Madison, Wisconsin. Samples of the harvested beans from the treatment plots and the "plot controls" were also analyzed. (Details of the sampling system at harvest are given in a previous paper, this report.[2]) Although the analyses of the tissues have not been completed, preliminary results suggest that marked changes in elemental content of both beans and vegetative tissue did occur in the fumigated plots, particularly at the higher SO_2 concentrations (Tables 1 and 2).

As expected, the greatest differences in leaf tissue concentrations between the fumigated and unfumigated plots were in sulfur levels (Figure 1). By the final sampling date (August 29) leaf sulfur concentrations in the high plot were about 4-1/2 times higher than those in the control plot, while those in the medium plot were 3 times higher than the control values. Smaller increases in S occurred in pods and seeds; stems are still being analyzed. On a ground area basis the total sulfur content of soybean leaves, pods, and seeds from the high plot was 2.9 g/m^2; the medium plot had 3.1 g/m^2, and the control plot 1.7 g/m^2. The high plot contained less total sulfur than the medium plot because the plants were considerably smaller.

At harvest time the beans from the high and medium plots also showed increased sulfur concentrations, but the increases were much smaller than those for the tissues; about 27% for the high plot and 12% for the medium plot (Table 2). On a ground area basis the beans harvested from the high plot contained 0.73 g/m^2 of sulfur, compared to 0.97 g/m^2 for the medium plot and 0.87 g/m^2 for the control plot. Again, the total sulfur content in the high plot is lower than the medium plot due to the reduced bean yield.

Table 1. Elemental concentrations in soybean tissues harvested on several dates from SO_2 fumigated plants. $LSD_{0.5}$ equals least significant difference ($p < .05$); n.s. equals no significant difference among plots. All data are % oven-dry weight.

Plot	Nitrogen	Sulfur	Phosphorus	Potassium	Magnesium
Leaves 14 July 1977					
High	4.49 ± 0.08	0.273 ± 0.011	0.345 ± 0.007	2.40 ± 0.04	0.618 ± 0.029
Medium	4.50 ± 0.07	0.273 ± 0.005	0.341 ± 0.003	2.16 ± 0.06	0.670 ± 0.016
Low	4.57 ± 0.02	0.250 ± 0.004	0.334 ± 0.005	2.25 ± 0.13	0.643 ± 0.035
Control	4.58 ± 0.04	0.218 ± 0.022	0.336 ± 0.004	2.28 ± 0.06	0.566 ± 0.007
$LSD_{.05}$	(n.s.)	0.039	(n.s.)	(n.s.)	(n.s.)
Leaves 27 July 1977					
High	4.01 ± 0.13	0.555 ± 0.013	0.280 ± 0.000	2.22 ± 0.07	0.531 ± 0.018
Medium	3.80 ± 0.04	0.398 ± 0.009	0.278 ± 0.003	2.09 ± 0.10	0.580 ± 0.021
Low	3.95 ± 0.09	0.285 ± 0.007	0.293 ± 0.008	2.13 ± 0.12	0.592 ± 0.012
Control	3.73 ± 0.04	0.233 ± 0.006	0.280 ± 0.000	2.38 ± 0.05	0.473 ± 0.008
$LSD_{.05}$	(n.s.)	0.027	(n.s.)	(n.s.)	0.048
Leaves 15 August 1977					
High	3.40 ± 0.07	0.733 ± 0.027	0.230 ± 0.001	1.85 ± 0.09	0.520 ± 0.025
Medium	3.68 ± 0.07	0.495 ± 0.021	0.253 ± 0.005	1.44 ± 0.03	0.585 ± 0.013
Low	3.47 ± 0.12	0.338 ± 0.023	0.253 ± 0.006	1.76 ± 0.06	0.551 ± 0.008
Control	3.57 ± 0.09	0.213 ± 0.008	0.277 ± 0.004	1.89 ± 0.06	0.450 ± 0.015
$LSD_{.05}$	(n.s.)	0.064	0.013	0.19	0.051
Leaves 29 August 1977					
High	2.74 ± 0.11	0.813 ± 0.010	0.192 ± 0.005	1.42 ± 0.06	0.474 ± 0.037
Medium	2.52 ± 0.07	0.525 ± 0.009	0.197 ± 0.005	1.31 ± 0.07	0.621 ± 0.013
Low	2.83 ± 0.03	0.283 ± 0.009	0.204 ± 0.003	1.34 ± 0.06	0.610 ± 0.020
Control	3.03 ± 0.04	0.178 ± 0.003	0.238 ± 0.004	1.46 ± 0.03	0.530 ± 0.010
$LSD_{.05}$	0.22	0.025	0.013	(n.s.)	0.069
Pods and Seeds 29 August 1977					
High	4.53 ± 0.24	0.363 ± 0.003	0.396 ± 0.006	2.10 ± 0.04	0.292 ± 0.013
Medium	4.94 ± 0.11	0.315 ± 0.005	0.404 ± 0.008	2.01 ± 0.03	0.289 ± 0.010
Low	4.75 ± 0.13	0.258 ± 0.011	0.392 ± 0.010	2.04 ± 0.05	0.301 ± 0.008
Control	4.74 ± 0.08	0.238 ± 0.008	0.403 ± 0.005	1.92 ± 0.02	0.295 ± 0.003
$LSD_{.05}$	(n.s.)	0.022	(n.s.)	0.10	(n.s.)

Table 2. Elemental concentrations in soybeans harvested from SO_2 fumigated and unfumigated plants. Data are oven-dry weight.

Element	Plot	Fumigated	Unfumigated	Difference, %	Significance, %
Nitrogen, %	High	6.30 ± 0.04	6.48 ± 0.09	-2.7	(n.s.)
	Medium	6.59 ± 0.04	6.74 ± 0.13	-2.1	(n.s.)
	Low	6.62 ± 0.03	6.57 ± 0.04	-0.9	(n.s.)
	Control	6.68 ± 0.05	6.76 ± 0.07	-1.2	(n.s.)
Sulfur, %	High	0.446 ± 0.005	0.350 ± 0.004	+27.4	($p < .001$)
	Medium	0.393 ± 0.004	0.353 ± 0.005	+11.3	($p < .001$)
	Low	0.328 ± 0.015	0.340 ± 0.025	-3.5	(n.s.)
	Control	0.340 ± 0.002	0.343 ± 0.005	-0.7	(n.s.)
Phosphorus, %	High	0.550 ± 0.007	0.547 ± 0.004	+0.6	(n.s.)
	Medium	0.544 ± 0.005	0.551 ± 0.007	-1.3	(n.s.)
	Low	0.536 ± 0.004	0.538 ± 0.003	-0.3	(n.s.)
	Control	0.547 ± 0.004	0.541 ± 0.004	+1.1	(n.s.)
Potassium, %	High	2.14 ± 0.02	2.09 ± 0.01	+2.6	(n.s.)
	Medium	2.03 ± 0.03	2.01 ± 0.01	+1.2	(n.s.)
	Low	2.05 ± 0.02	2.01 ± 0.02	+2.1	(n.s.)
	Control	2.02 ± 0.01	2.00 ± 0.01	+1.3	(n.s.)
Calcium, %	High	0.204 ± 0.002	0.191 ± 0.003	+6.7	($p < .01$)
	Medium	0.193 ± 0.002	0.200 ± 0.003	-3.5	(n.s.)
	Low	0.192 ± 0.004	0.200 ± 0.002	-3.6	(n.s.)
	Control	0.208 ± 0.003	0.215 ± 0.003	-3.2	(n.s.)
Magnesium, %	High	0.223 ± 0.002	0.252 ± 0.003	-11.3	($p < .001$)
	Medium	0.235 ± 0.003	0.253 ± 0.002	-7.2	($p < .01$)
	Low	0.242 ± 0.002	0.252 ± 0.001	-3.8	($p < .05$)
	Control	0.238 ± 0.001	0.246 ± 0.002	-2.9	($p < .05$)
Copper, ppm	High	12.5 ± 0.4	9.6 ± 0.8	+30.0	($p < .01$)
	Medium	10.0 ± 0.5	9.3 ± 0.6	+6.8	(n.s.)
	Low	9.6 ± 0.7	9.4 ± 1.0	+2.2	(n.s.)
	Control	8.7 ± 0.4	9.0 ± 0.8	-4.0	(n.s.)
Zinc, ppm	High	44.9 ± 0.6	40.3 ± 0.4	+11.4	($p < .001$)
	Medium	42.3 ± 0.4	41.0 ± 1.7	+2.8	(n.s.)
	Low	40.2 ± 0.5	38.7 ± 0.4	+3.9	(n.s.)
	Control	36.6 ± 0.5	35.4 ± 0.9	+3.6	(n.s.)
Manganese, ppm	High	18.0 ± 0.4	20.4 ± 0.4	-11.4	($p < .01$)
	Medium	20.6 ± 0.2	20.5 ± 0.6	+0.4	(n.s.)
	Low	18.4 ± 0.3	18.1 ± 0.3	+1.4	(n.s.)
	Control	16.2 ± 0.3	15.8 ± 0.5	+2.2	(n.s.)

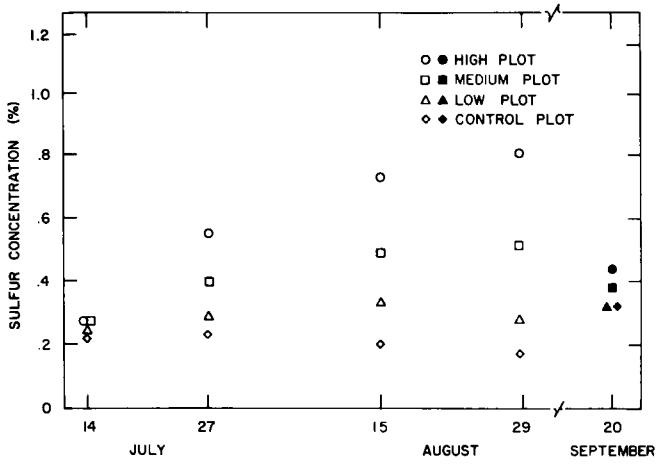

FIG. 1.--Sulfur content of soybean tissues on various sampling dates. Open figures, leaves; solid figures, beans. (ANL Neg. 149-78-249)

A major thrust of the Argonne SO_2 Effects Program is to estimate the actual dose of SO_2 taken up by the plants in the fumigation plots and to attempt to relate this does to observed injury. This dose (uptake) can be estimated directly by determining the increase in sulfur content of fumigated plants or indirectly by utilizing micrometeorological techniques.[3] The micrometeorological data from the 1977 field experiments are still being analyzed, but a preliminary estimate of the "excess" sulfur content of the plants on the medium and high plots has been computed by comparing the actual sulfur content of the fumigated plants (excluding stems and roots) to the amount that plants the same size would have contained as control-plot concentrations. For example, at control-plot S concentrations the high-plot plants (leaves, pods and seeds only) would have contained 1.15 g S/m^2 on August 29. Since the high-plot plants actually contained 2.9 g/m^2 on this date, this represents an excess of 1.75 g/m^2. Calculated in the same way, the excess for the medium plot plants on August 29 was 1.4 g S/m^2. (Since these numbers exclude stems and roots, which may also contain elevated sulfur levels, they represent minimum values for "excess" sulfur in the plants; the actual increases may be somewhat higher.) Similar calculations were made for the harvested beans, but the numbers are much smaller; the excess S in the beans from the high plot is only 0.18 g/m^2, while the excess for the medium plot is 0.13 g/m^2. Thus, less than 10% of the total "excess" sulfur taken up during the fumigations is translocated to the harvested crop; the rest remains in the chaff, shed leaves, or roots and is eventually added to the soil.

In addition to the increase in sulfur, there were several other elements whose concentrations in leaf tissue varied significantly among the treatment plots (Table 1). Some of these variations may be due to the SO_2 treatment (e.g., the low magnesium levels in the high plot), but most appear to be due to soil variations among the treatment plots. There were also some significant variations in the elemental content of the beans harvested from the various plots. Since in this case each plot was compared to its own nearby control, it is likely that the observed increases in Ca, Cu, and Zn and decreases in Mg and Mn in the high plot do represent changes due to the SO_2 treatment.

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INFLUENCE OF SULFUR DIOXIDE FUMIGATION ON PATHOGEN DEVELOPMENT IN FIELD-GROWN SOYBEANS: A PRELIMINARY STUDY

J. E. Miller, R. N. Muller, and D. G. Sprugel

In addition to direct effects of air pollutants on plant species, it is conceivable that air pollutant induced stress may affect the normal balance of plant pathogens within a field. Certain fungal pathogens have been shown to be sensitive to air pollutants such as SO_2 and ozone; on the other hand, it is well established that certain fungi more readily infect weakened or damaged tissues. For these reasons it was decided to conduct a general survey of the incidence of common soybean pathogens throughout the 1977 growing season in the SO_2 treatment plots described in the first paper of this series.

Plant samples were taken at random at approximately biweekly intervals from June 27 through August 30 from the control and three treatment plots. The treatment plots were exposed to 92, 236, and 706 ppb of SO_2 (geometric means) and are designated the low, medium, and high plots, respectively. The roots, stems, pods, and 9-mm discs cut from the leaves were washed for 2 hr in water, soaked for 2 min in 0.25% sodium hypochlorite, and rinsed twice in distilled water. Four pieces of each plant part were aseptically placed in culture plates containing potato-dextrose agar and incubated for 7 days at 25°C, at which time the percentage occurrence of microorganisms was recorded. Seed samples collected at harvest were similarly treated.

The accumulated data for all sampling periods showed no statistically significant effects of SO_2 treatment on the mean percentage recovery of the total or individual fungi (Table 1). However, at the higher SO_2 treatment level there was a slight trend toward more recoverable total fungi (Alternaria, Fusarium, and Stemphylium), although Phomopsis may have decreased slightly. These trends were not consistent at individual sampling dates, except that the number of Phomopsis recovered from the leaves was always substantially higher in the control and low SO_2 treatment plot than in the medium and high plots. This may indicate that the higher SO_2 exposures were reducing leaf infection by Phomopsis. As would be expected, the total fungi recovered from all vegetative

Table 1. Mean percentage recovery of various fungi and total fungi from Wells soybeans exposed to four levels of SO_2

Treatment ppb SO_2	Fungal genera[a]						Total Fungi[b]
	Alt	Fus	Pho	Phm	Ste	Ver	
Ambient	53.8	9.1	12.5	1.2	0.14	18.3	97.7
92	55.0	7.1	7.4	7.0	0.35	16.6	99.8
236	55.8	10.2	9.5	5.1	0.84	18.0	104.5
706	57.4	11.3	5.8	4.3	1.32	18.3	102.2
$LSD_{.05}$	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

[a]Alt = *Alternaria*; Fus = *Fusarium*; Pho = *Phomopsis* (*Diaporthe phaseolorum* var. *sojae*); Phm = *Phoma*; Ste = *Stemphylium*; Ver = *Verticillium*.

[b]Total fungi exceeds 100% because of presence of more than one isolate per test piece.

Table 2. Mean percentage recovery of various fungi and total fungi from Wells soybean seed from the four treatment plots

Treatment ppb SO_2	Fungal genera[a]							Total Fungi
	Alt	Asp	Cer	Col	Fus	Pho	Phm	
Ambient	8.6	5.0	0.6	0	0	46.6	0.6	61.0
93	11.0	3.0	1.0	0	0.1	39.6	2.0	57.6
236	6.6	3.0	0	1.0	1.0	29.0	4.0	44.6
706	19.6	0.6	0	0.6	4.0	44.6	1.6	70.6
$LSD_{.05}$	5.3	2.8	n.s.	n.s.	n.s.	10.3	n.s.	14.0
$LSD_{.01}$	7.4	n.s.	n.s.	n.s.	n.s.	14.4	n.s.	19.6

[a]Alt = *Alternaria*; Asp = *Aspergillus*; Cer = *Cercospora*; Col = *Colletotrichum*; Fus = *Fusarium*; Pho = *Phomopsis* (*Diaporthe paseolorum* var. *sojae*); Phm = *Phoma*.

tissues increased at each successive sampling date throughout the summer.

The bioassay of seeds harvested when the plants were mature showed variable and only occasionally significant differences in the recovery of individual or total fungi between the control and SO_2 treatment plots (Table 2). For example, Aspergillus declined with increasing SO_2 levels, while Fusarium increased slightly. Phomopsis declined in the medium plot relative to the control, but not in the high plot. The total recoverable fungi also were reduced in the medium plot relative to the control but were elevated in the high plot.

The results of this first year's study are not conclusive but lend support to the contention that SO_2 may modify soybean-pathogen interactions. Future studies will utilize more intensive sampling techniques in order to account for the expected plant and field variability.

RESPONSE OF SOYBEANS TO ACID PRECIPITATION ALONE AND IN COMBINATION WITH SULFUR DIOXIDE

P. M. Irving and J. E. Miller

Energy-related air pollution is a world-wide problem of increasing complexity. Sulfur and nitrogen oxide emissions, produced by the combustion of fossil fuels, have given rise to increased SO_2 and NO_x concentrations in the atmosphere over much of the northeastern United States and northern Europe. Transformation products of SO_2 and NO_x sulfate and nitrate aerosols, can remain in the atmosphere until they are removed by rain, leading to acid precipitation at great distances from the source of pollution.[1]

A preliminary study of the authors indicates that acid precipitation may become a problem in the Midwest. Natural precipitation was collected at Argonne from April 19, 1977 to October 22, 1977. Chemical analyses indicated the presence of strong acids in all samples. The pH of the rain varied from 3.48 to 5.90, averaging 4.15. Hydrogen ion concentration averaged 78.8 microequivalents per liter. These values indicate that precipitation in the Chicago area is similar to that of the northeastern United States, where acid rain is considered a serious environmental problem. The average annual pH of rainfall at Hubbard Brook was 4.0 to 4.2 during the period 1964 to 1974, while the hydrogen ion concentration averaged 73.9 microequivalents per liter.[2] These analyses indicate a need for further study of precipitation chemistry in the Midwest coupled with research efforts to determine the effects of this acidity on the agricultural industry of the area. Very little has been done concerning the effects on productivity of acid precipitation administered during the entire life cycle of a plant. Interactive effects of pollutants occurring in combination must also be considered. Accordingly, the following study was undertaken.

This study was incorporated into the open air fumigation system as described in a previous paper.[3] Two 16- × 20-ft subplots, one exposed to acid precipitation (pH 3.0) and the other to control precipitation (pH 5.5), were placed in each of the control and high (786 ppb SO_2) fumigation plots. The precipitation simulant and apparatus were designed to reproduce as closely as possible the

physical and chemical characteristics of natural rainfall. The precipitation simulant was applied a total of eight times during the growing season beginning July 20, 1977, and continuing weekly to September 5, 1977. Twenty-four SO_2 fumigations took place between July 13 and August 29, 1977.

Although not statistically significant, the results indicate that simulated precipitation with a pH of 3.0 caused an apparent reduction in soybean seed yield as compared to simulated precipitation with a pH of 5.5 in both the control and high SO_2 plots (Table 1). The data suggest that the apparent yield reduction may be due, in part, to a lower dry weight per seed produced by plants treated with the acid simulant (Table 1). Plants in the control SO_2 plot receiving acid precipitation simulant exhibited higher photosynthetic rates, as measured by incorporation of $^{14}CO_2$, and lower diffusive resistances than plants receiving control simulant (Table 2). The apparent increase in effect through time, suggests that acid precipitation affects plant metabolism in a cumulative manner. Chlorophyll content was 29% higher ($p < 0.1$) in plants receiving acid simulant than in control plants near the end of the growing season. This suggests a delay in senescence in the acid treated plants. There was an erosion of leaf epicuticular wax, as determined by extraction, due to both control and acid precipitation, although the data, which were not statistically significant,

Table 1. Average dry weight ± standard deviation

	grams per row[a]	grams per seed[b]	grams per row[a]	grams per seed[b]
Control ppt	1193.56 ± 39.74	0.1693 ± 0.0047	679.44 ± 108.48	0.1309 ± 0.0072
No ppt	1151.78 ± 178.64	0.1705 ± 0.0168	722.79 ± 81.92	0.1310 ± 0.0161
Change, %	4 (n.s.)	-0.71 (n.s.)	6 (n.s.)	0.08 (n.s.)
Acid ppt	1146.97 ± 78.52	0.1160 ± 0.0053	617.62 ± 122.21	0.1207 ± 0.0059
No ppt	1277.65 ± 107.52	0.1722 ± 0.0126	685.42 ± 42.48	0.1310 ± 0.0174
Change, %	-11 ($p < .10$)	-3.73 (n.s.)	-11 (n.s.)	-8.53 (n.s.)

[a]Determine by averaging 4 rows per plot.

[b]Determine by averaging 100 seeds per row, 4 rows per plot.

Table 2. Photosynthetic rate and diffusive resistance, means ± S.D.

	Control ppt	Acid ppt	Change, %
Photosynthetic rate, mg $CO_2/dm^2/hr$			
0 ppm SO_2			
13 August 1977	25.42 ± 6.25	27.80 ± 4.35	9 (n.s.)
18 August 1977	15.75 ± 4.07	17.82 ± 3.33	12 (n.s.)
6 September 1977	9.67 ± 3.16	11.67 ± 2.72	17 ($p < 0.2$)
0.8 ppm SO_2			
13 August 1977	11.78 ± 4.49	11.83 ± 4.16	0.4 (n.s.)
Diffusive resistance, sec/cm			
13 August 1977	1.61 ± 0.38	1.66 ± 0.41	3 (n.s.)
18 August 1977	3.24 ± 0.75	3.05 ± 0.70	-6 (n.s.)
6 September 1977	4.41 ± 2.09	3.97 ± 0.96	-11 (n.s.)

indicate a higher degree of leaching by the acid simulant (20%) than the control simulant (9%) in the control SO_2 plot. This increased erosion due to acidity could result in greater transpirational water loss and could also decrease leaf resistance to pathogen infection. The data also suggest that oil content is lower (4%) in seeds produced by plants receiving acid simulant as compared to control plants.

These results suggested that acid precipitation may alter the physiological processes of soybeans. It is possible that this is caused by changes in cellular pH through the accumulation of H^+ and SO_4^{2-} ions, which may, in turn, affect enzyme or hormonal activity at sufficiently high pollutant concentrations.[4,5] Initial enzyme changes can produce many effects on the molecular level, which, in turn, could alter physiological phenomena such as those seen in this study.

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ANALYSES OF ECHO-LOCATION DATA FROM POWER PLANT STUDIES

S. A. Spigarelli, W. Prepejchal, and I. P. Murarka*

Through the combined use of thermal plume mapping and "acoustic sampling" of fish distribution we have investigated the magnitude of fish attraction to thermal discharges into Lake Michigan. This nondestructive sampling method allows rapid observation of fish distribution patterns and provides data that can be used to quantify temperature selection, numbers and biomass of fish that are attracted to thermal discharges. Since 1973, when this technique was first proposed by ANL[1] for use in effluent areas, numerous agencies have tested its validity, and the technique is now being incorporated into environmental monitoring programs at power plants and into research programs aimed at describing fish distribution in Lake Michigan.

The methods of echo-surveying in discharge areas have been reported elsewhere.[1,2] Determinations of volumes of water sampled are based on distance sampled along a depth contour and the effective sampling volume, which is dependent on the transducer beam angle. Echo traces (fish) can be counted manually or through the use of computer techniques to integrate recorded signals.[3,4] For purposes of statistical comparisons, sampling runs along a contour are divided into subsections (cells) of equal length if possible (unequal length cells occasionally are necessary to avoid recording densities = 0). The number of fish observed in each cell is recorded as a total and as the number per depth and temperature stratum within the cell. At this point in the data handling process, a number of analytical procedures may be adopted. If the data are not distributed normally (common with schooling fishes), various transformations such as log or square root may be applied to normalize the data. Comparisons of fish distribution patterns (by temperature and depth) can be made between locations (plume and reference; north versus south basins of Lake Michigan, etc.) by polynomial regression techniques. Polynomial fits of the

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relationship between fish density and sampling time within each year will provide mean quantitative estimations of density and regression coefficients that can be used to compare locations and time periods. Statistical tests comparing the coefficients can be used to establish the significance of differences due to fish attraction or avoidance.

The above procedures allow a general description of differences in fish distribution between thermal plume and reference areas. However, it is not possible to identify localized areas of high density by relating fish numbers to depth or temperatures. For instance, it is tempting to disregard low fish densities in ambient temperature waters surrounding a plume, but careful inspection of spatial patterns may indicate high densities of fish in close proximity to temperature interfaces and steep temperature gradients. Consequently, we are utilizing three-dimensional graphics to identify locations of high density. Examples of this graphical method are given in Figures 1 and 2. The density values in these figures are not transformed and represent actual values in the total water column along each depth contour. By comparing the differences in spatial orientation and densities of fish between plume and reference regions, the three-dimensional analysis allows a definition of the number of fish in close proximity to the plume.

An important aspect of fish attraction to thermal discharge areas is their temperature selection as a function of time (diel and seasonal), location (north or south basin of Lake Michigan) and discharge type (channel or submerged diffuser). The echo-location technique provides a means of studying temperature selection in the field that is equivalent to accepted laboratory techniques; i.e., frequency of occurrence (density) at each available temperature is determined and plotted to provide a statistical interpretation of selected temperature (mode = selected). Examples of this procedure are presented in Figures 3 and 4. This survey was conducted during the period in which alewife populations congregate inshore prior to spawning. In the reference area fish densities were ten times higher in the limited volume of water at 9 to 10°C (the maximum ambient temperature) than in large volumes of water at 7 to 9°C. In the plume region (including ambient water surrounding the plume) fish selected the

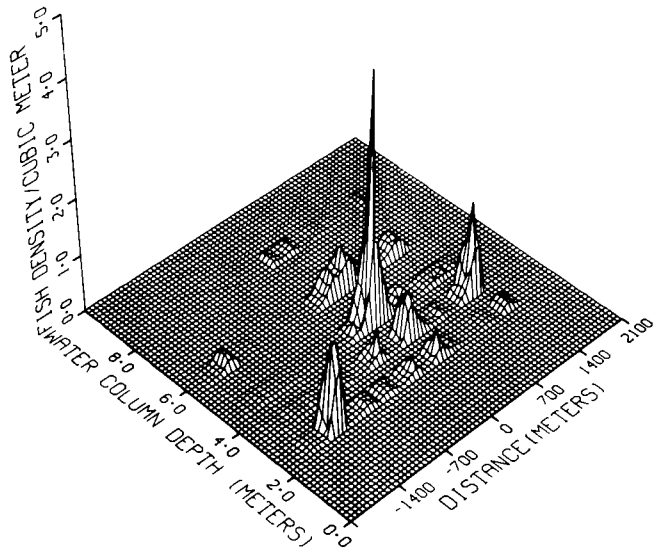

FIG. 1.--Three-dimensional map of fish distribution in the Point Beach thermal plume. Fish densities are summed for the water column (19 June 1974).

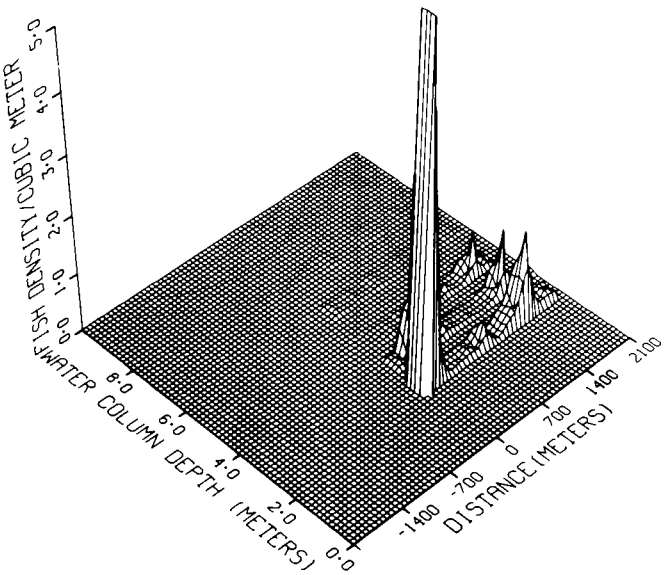

FIG. 2.--Three-dimensional map of fish distribution in an unheated reference area. Fish densities are summed for the water column (18 June 1974).

9 to 11°C range, which included the plume-ambient temperature interface. On this date, the total plume area density was significantly greater than the reference area density, but the majority of fish were oriented to the edges of the plume, rather than to the high temperature regions.

In addition to the description of temperature and spatial orientation of fish, echo-location data provide a means of relating salmonid behavior in plumes to forage fish densities and of modeling the potential for effects on salmonid energetics and forage consumption.[5]

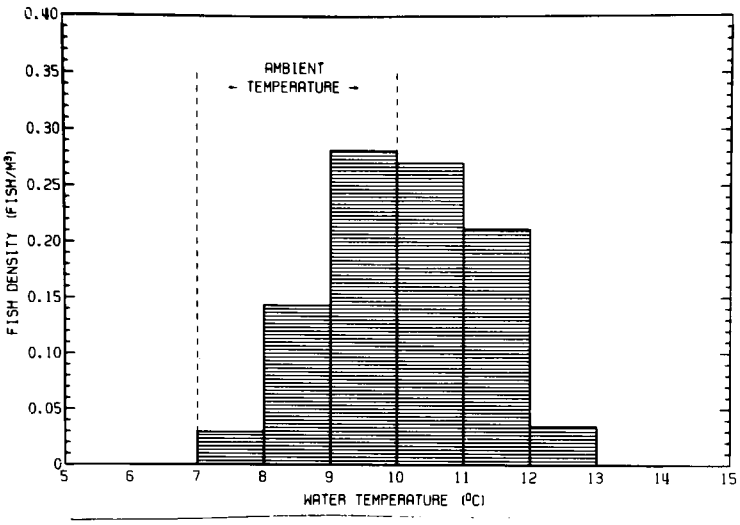

FIG. 3.--Frequency distributions of fish at each available water temperature in the Point Beach plume.

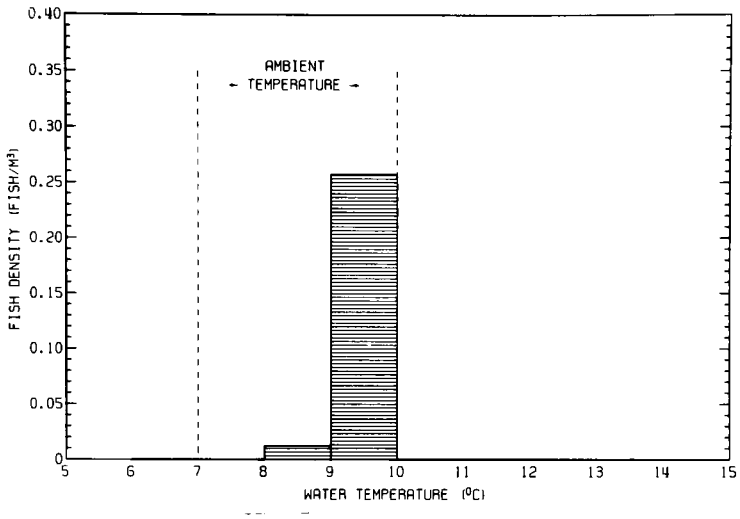

FIG. 4.--Frequency distributions of fish at each available water temperature in an unheated reference area.

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BODY TEMPERATURES AND ACCLIMATION OF RAINBOW TROUT IN A THERMAL PLUME

S. A. Spigarelli and M. M. Thommes

Laboratory studies of temperature selection by rainbow trout have resulted in highly conflicting reports on the final preferred temperature and the functional relationship between acclimation and selected temperatures for this species. Preferred temperature theory predicts that ultimately fish will acclimate to their final preferred temperature, if available in gradients. Since any analysis of temperature effects requires accurate determinations of temperature selection and acclimation under field conditions, the conflicting results of laboratory studies are of little value until corroborated by field studies.

During the course of a sport fishing census at the Point Beach Nuclear Plant[1] we obtained measurements of the body temperatures of 754 rainbow trout. These data were statistically analyzed to determine (1) the temperature selection and acclimation, and (2) the influence of season, water temperature and fish size on temperature responses of this species in nature.

Despite large scale temporal variability in natural water temperatures and in catch rates of rainbow trout, our results show a statistically significant bimodal distribution of body temperatures (Figure 1) for all rainbow trout. The mode at 19°C corresponds to the final preferred temperature reported in two of the many laboratory studies[2,3] and with the limited field data.[4] Comparisons of body temperatures with fish size showed that the 19°C mode was representative of small rainbow trout (< 1 kg), while the 15°C mode represented fish larger than 1 kg. This size-related difference in temperature selection is important because the majority of laboratory studies include only small fish.

A summary of modal body temperatures and estimated mean acclimation temperature for weight and season groups of rainbow trout is presented in Table 1. Acclimation temperatures were estimated for each fish by assuming a functional relationship between selected and acclimation temperatures[2] and by assuming that each body temperature was a selected temperature. Excess acclimation temperature for each fish was calculated by subtraction of ambient

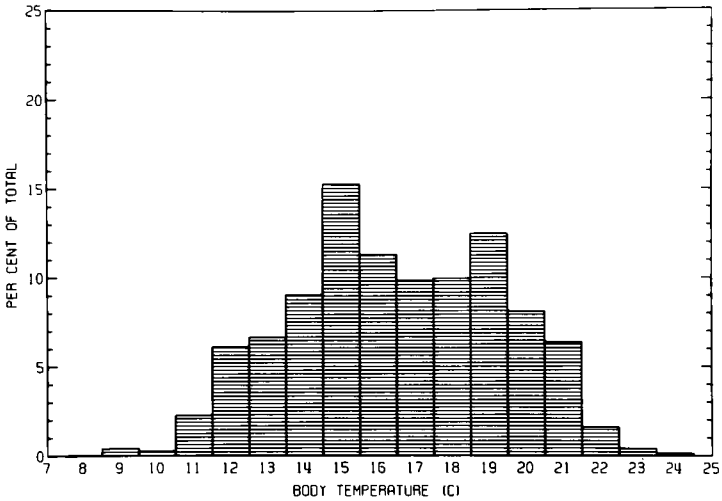

FIG 1.--Frequency distribution of rainbow trout body temperatures (1972 and 1973).

Table 1. Summary of body temperature data for rainbow trout caught at Point Beach in 1972—1973.

Group	N	Modal T_b °C	% plume acclimated (range)	Mean excess acclimation (range)°C
Total	754	15;19	28—76	3.2—5.6
Spring	35	15	37—86	3.0—4.6
Summer	282	19	43—90	4.1—6.2
Fall	437	15	17—67	2.4—5.0
Small (<1 kg)	287	19	51—93	4.3—6.0
Medium (1—2.5 kg)	175	15	23—75	2.6—5.1
Large (>2.5 kg)	301	15	10—61	2.1—4.7

acclimation temperature from estimated fish acclimation temperature. These data show the size-related differences in body temperature, seasonal shifts in selected temperature, and the extent to which rainbow trout acclimate to thermal plumes in Lake Michigan.

At least 28% and as high as 76% of the rainbow trout caught by fishermen at Point Beach were acclimated to elevated temperatures. Small fish and those caught during the summer showed the highest percentages of plume acclimation and the highest excess acclimation temperatures. Mean excess acclimation temperatures on the order of 5 or 6°C indicate substantial exposure to elevated temperature and the potential for significant effects on energetics, growth,

food consumption, and accumulation of toxic materials by fish residing in thermal plumes.

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ENERGETIC COSTS OF THERMAL PLUME EXPOSURE TO BROWN TROUT

K. Derickson,* S. A. Spigarelli, and M. M. Thommes

Studies of fish attraction and exposure to thermal discharges into Lake Michigan have shown species-specific seasonal periods of attraction.[1] The major forage species are attracted to and concentrate in thermal plumes during spring (smelt spawning), summer (alewife spawning), and fall (smelt and alewife young of the year).[2] High densities of salmonid fishes are observed in thermal plume areas during each season, except when intake temperatures approach final selected temperatures for these species (16–20°C). Through extensive use of underwater radiotelemetry,[3] we have measured seasonal temperature responses and exposures of brown trout in the Point Beach Nuclear Plant discharge area.

Given these observations, a preliminary analysis was done to estimate the additional energetic costs of plume residence. Body temperature data for a 1.59 kg female and a 2.72 kg male were used to compute energetic needs for a 410 and 452 hr tracking period in February and April, respectively. The body temperature data were tabulated to determine the number of hours spent at various temperatures and using energy budget equations from Elliott[4] the caloric requirements under maintenance (no growth) and optimum conditions (maximal growth) were estimated for the two tracking periods. The total caloric requirements were broken down to compare the energy needs at ambient water temperatures to those at plume temperatures. The additional energy costs created by the periods of plume residence were computed in three ways. First, the calories required per hour at plume temperatures were divided by the calories required per hour at ambient temperature (physiological cost). Second, the milligrams of body lipids required per hour to fulfill energy needs at average plume temperatures were divided by the milligrams of lipid per hour at ambient temperatures (physiological cost). Third, the milligrams of prey fishes (alewife and rainbow

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smelt) needed per hour to meet energy needs at plume temperatures were divided by ambient hourly requirements (environmental cost).

Table 1 shows the calculated energy requirements and the physiological and environmental costs for these two fish at ambient and plume temperatures under maintenance and optimum conditions. From these data it is obvious that the time spent at plume temperatures was very costly, particulary during winter (1.59 kg female). During February, one hour of exposure to average plume temperatures required 6 to 14 times as much energy as an hour at ambient temperatures. To fulfill this additional energy need, a fish would have to utilize 6 to 14 times as much prey fish or body lipids as a fish at ambient temperatures. The additional cost to the spring fish (2.72 kg male) was only about twice the ambient cost.

The February track data show that the female spent at least 30% of its time at temperatures above ambient, while the April data show that the male spent at least 14% of its time at temperatures above ambient. Why these fish are attracted to the plume is not clear. However, during the winter months it is probably a rheotactic or thermal response since prey densities are estimated to be extremely low in and outside the plume ($\ll$ 1 fish/1000 m^3) during this period. Attraction during the winter months suggests that brown trout must mobilize body lipids to fulfill the additional energy costs. Attraction to the plume in the spring may be due to greater prey densities in the plume (estimated to be twice ambient densities)[2] and rheotactic and thermal responses. Because the spring fish spent less time in the plume than winter fish and because prey densities are greater in the plume during spring, it is possible that the net energy available for growth is greater in spring-plume fish than in those that do not enter the plume.

A computer simulation model is being developed that will utilize body temperature data from tracked fish to compute seasonal energy budgets. This model will compare the seasonal energy needs of these fish with seasonal prey densities to ascertain if sufficient energy is available to fulfill these needs. Short-term energy deficits or surpluses will be used to estimate long-term impacts on the population by converting the former into growth and offspring

Table 1. Caloric requirements, physiological and environmental costs associated with thermal plume residence by brown trout.

	Female (1.59 kg)	Male (2.72 kg)
Track dates	2/9—3/2/77	4/13—5/3/77
Track hours	410	452
Hours at ambient temperature	276	391
Hours at plume temperature	134	61
Ambient water temperature, °C	2	6
Mean body temperature in plume, °C (range)	13 (5—18)	11 (7—14)
Physiological costs		
A. Metabolism, calories/hr		
1. Maintenance conditions		
a. ambient	79	284
b. plume	469	524
c. cost index (2/1)	5.9	1.8
2. Optimum conditions		
a. ambient	77	615
b. plume	1064	1196
c. cost index	13.8	1.9
B. Body lipids, mg/hr		
1. Maintenance conditions		
a. ambient	11	39
b. plume	65	72
c. cost index	5.9	1.8
2. Optimum conditions		
a. ambient	11	85
b. plume	148	166
c. cost index	13.4	2.0
Environmental costs, mg forage/hr		
1. Maintenance		
a. ambient	55	197
b. plume	326	364
c. cost index	5.9	1.8
2. Optimum conditions		
a. ambient	54	428
b. plume	740	833
c. cost index	13.7	1.9

units. Once refined and tested, this model will provide a quantitative procedure for assessing thermal impacts to fish that presently does not exist to the impact assessor. The present qualitative procedure of assessment generally has considered acute affects and therefore the conclusions about thermal impacts (negligible effects) differ from those in this preliminary study of potential chronic affects.

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ACCUMULATION OF TOXIC MATERIALS BY THERMAL PLUME RESIDENT BROWN TROUT

G. P. Romberg, S. A. Spigarelli, W. Prepejchal, and M. M. Thommes

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The results of field studies suggest that Lake Michigan trout and salmon may experience increased accumulation of toxic materials due to their exposure to elevated temperatures at thermal discharges.[1,2] Since large numbers of trout encounter themal plumes,[3,4] and many of these fish are harvested by sport fishermen,[5] a significant increase in toxicant accumulation would constitute a human health hazard that needs further study. Consequently, we are designing a field laboratory in which a series of experiments will be conducted to quantify the effect of plume residence on growth and the uptake of toxic materials. Environmental conditions will be simulated by using actual intake and discharge water from a coal-fired power plant and by feeding Lake Michigan alewife to trout.

Since considerable basic information is needed to design a comprehensive set of experiments and a research facility, we conducted a pilot study at the Point Beach Nuclear Plant in 1977. This study provided information regarding (1) the logistics of maintaining fish in tanks at simulated environmental conditions, (2) the predominant toxicants in Lake Michigan water and fish, (3) the appropriate analytical techniques for each toxicant, (4) variability in growth and uptake rates, (5) length of time to equilibrium, and (6) the ultimate concentration factors (fish concentration/food concentration) at equilibrium.

In the pilot study, 17 brown trout (mean weight = 258 g) were obtained from a hatchery and transported to Point Beach where they were placed in a 125-gallon tank supplied with intake water. Test fish were fed chopped alewife to satiation once daily. All trout were weighed initially and again after 15 days when three fish were sacrificed. Fish were reweighed again after another 26 days when four more fish were sacrificed. Five of the remaining ten fish were then transferred to a second tank supplied with discharge water ($\leq 21°C$). Fish in both tanks were periodically reweighed during the next 110 days after which time the pilot study was terminated.

The specific growth rates of test fish were not statistically different between groups through the first 97 days of the experiment, but that of fish held at ≤ 21°C (discharge temperature) declined during the last 30 days (Figure 1). The combination of high temperature and less than maximum ration contributed to the decline in growth rate of this group.

Analytical procedures for measuring organic toxicant levels in fish are currently being developed (ANL Chemical Engineering Division). As a part of this analytical development, selected fish samples from this experiment were analyzed by the Bureau of Sport Fisheries Laboratory (Ann Arbor, Michigan) for p.p' DDE (DDT residues) and PCB's. Measured values for two alewife samples and six individual trout (3 hatchery fish and 3 experimental fish after 15 days) are reported in Table 1. The levels of PCB's in hatchery fish were below detection limits (< 0.2 ppm), but after only 15 days of feeding on Lake Michigan alewife the mean whole body level of trout rose to 0.89 μg/g. Concentrations of p.p' DDE increased by nearly an order of magnitude over this period. At this rate of uptake about three months would be required for the trout to reach 90% of the equilibrium concentration of PCB, if the final concentration factor (trout/alewife) equals one. Available information on PCB concentrations in Lake Michigan brown trout indicates an average concentration factor of 1 to 2. Thus, an experiment of at least 4 to 5 months' duration would be necessary to document temperature effects on toxicant accumulation.

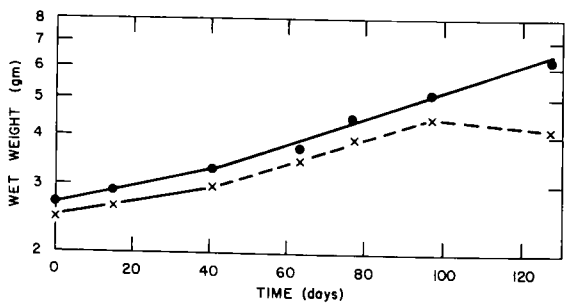

FIG. 1.--Average wet weight as a function of time for two groups of brown trout (5 fish each) fed to satiation once daily. Initially (41 days) both groups were exposed to intake conditions (solid line) with an average temperature of 12.8°C. Subsequently one group remained at intake temperatures (average = 14.9°C) while the other group was exposed to discharge conditions (dashed line) which averaged 4.0°C warmer. (ANL Neg. 149-78-252)

Table 1. Results of preliminary analyses of samples from pilot experiment (mean ± S.E.).

Species	Type	N	% lipid	p.p' DDE, μg/g	Total PCB, μg/g)
Brown trout	hatchery	3	7.4 ± 0.2	0.04 ± 0.003	≤ 0.20
	experimental	3	7.0 ± 0.3	0.23 ± 0.01	0.89 ± 0.08
Alewife	Lake Michigan	40	3.6	0.74	3.21
	Lake Michigan	40	4.0	0.69	2.69

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TRACE ELEMENTS IN LAKE MICHIGAN FISHES

S. A. Spigarelli and M. M. Thommes

Samples of Lake Michigan fishes have been collected by ANL at irregular intervals since 1968. The majority of these samples were analyzed for radioactive contaminants, but a few were analyzed for trace elements by the neutron activation method. Table 1 summarizes the results of trace element analyses on Lake Michigan fishes.

Although it is not possible to draw firm conclusions about trends in trace element concentrations from these limited data, they do provide some insight into the importance of factors that may affect pollutant accumulation and deposition by fish. For instance, there seem to be differences in concentrations of Co, Cu, As, Cd, and Sb between liver samples of immature (age III) coho salmon collected in the spring and mature (age III) fish collected the following fall. These differences could be due to a number of factors, the most likely being the size-related seasonal differences in diet and metabolic state of coho salmon. Age III coho weigh approximately 1 kg in early spring (April) and tend to feed on benthic invertebrates such as Pontoporeia affinis and Mysis relicta. In early summer, age III coho switch to a diet consisting primarily of alewife and smelt and grow rapidly until the fall spawning period when feeding essentially stops and adults begin to metabolize stored energy resources.

The data on trace element concentrations in coho tissues during the fall spawning period (when a large sport catch occurs) indicate relatively high concentrations of (1) As, Cd, and Rb in muscle, (2) As and Br in gill, (3) Se and As in gonads, and (4) various elements in specific organs such as liver, kidney, and spleen. Specific concentrations of toxic elements in inedible tissues are important from the standpoint of identifying appropriate sample types for further study and of relating body-tissue burdens to possible direct toxic effects on fish and transfer to man as a consumer. Estimates of predator–prey bioconcentration factors are presented in Table 1. Spring salmon muscle is slightly enriched (2.1 times) in As and significantly enriched (8.7 times) in Cd over

Table 1. Summary of results of trace element analyses on Lake Michigan fishes (all values are ppm wet weight).

	Co	Cu	Zn	As	Br	Cd	Cr	Se	Rb	Sb	Hg[c]
1968—1969[a]											
Lake trout liver	0.036	21.00	26.35	0.018	2.62	0.06	--	--	--	--	0.19
Bloater liver	0.040	7.40	44.05	0.012	0.13	0.04	--	--	--	--	0.25
Whitefish liver	0.036	8.50	25.25	0.021	0.27	0.09	--	--	--	--	0.07
Smelt liver	0.013	1.50	12.30	<0.021	0.14	0.07	--	--	--	--	0.14
Alewife (whole)	0.023	0.68	16.15	0.023	0.11	0.05	1.10	--	--	--	0.49
Pontoporeia	0.019	2.27	7.51	0.777	5.66	0.03	1.20	--	--	--	0.10
1972											
Spring coho salmon[a]											
liver	0.014	8.89	25.27	0.65	1.36	0.13	--	0.68	4.96	0.036	--
muscle (est.)	0.0008	1.04	5.05	1.63	0.97	0.26	--	0.32	6.20	0.001	--
Fall coho salmon[b]											
liver	0.032	3.48	18.53	0.22	1.44	0.07	<0.09	0.62	4.03	0.070	--
kidney	0.063	0.68	11.31	0.11	1.77	0.32	--	0.24	2.91	0.004	--
spleen	0.009	0.36	17.62	1.08	1.23	0.93	<0.09	0.51	4.40	0.022	--
heart	0.002	1.67	14.88	0.87	1.29	0.63	<0.08	0.20	5.37	0.002	--
skin	0.002	0.38	8.92	0.19	0.30	0.12	<0.18	0.38	<1.45	0.001	--
gills	<0.002	0.23	13.25	1.32	3.11	0.13	--	0.58	<3.35	0.014	--
eggs	0.003	1.26	14.21	0.68	0.64	0.06	0.04	1.10	2.13	0.008	--
testes	0.003	0.99	4.96	1.23	1.69	0.009	0.02	--	2.51	0.002	--
muscle	0.002	0.41	3.70	0.49	1.06	0.15	<0.13	0.30	5.20	0.002	--
liver/muscle	16	8.5	5	0.4	1.4	0.5	~1	2.1	0.8	35	--
Bioconcentration Factors (predator/prey)											
fall salmon/whole muscle / alewife	0.08	0.6	0.2	21	9.6	3					
spring salmon/Pontoporeia muscle /	0.05	0.5	0.7	2.1	0.2	8.7					
fall salmon/smelt liver / liver	2.5	2.3	1.5	10	10	1					
lake trout/smelt liver / liver	2.8	14	2.1	1	18.7	1					

[a] Collections near Saugatuck and Muskegan, Michigan, and Waukegan, Illinois.(1)

[b] Platte River, Michigan.

[c] Whole fish analyses.(2)

Pontoporeia (a major food source for immature salmon). Fall salmon muscle is enriched in As (21 times) and Br (9.6 times) compared to whole alewife, the principal food of adult salmon. Livers of fall salmon show enriched concentrations (10 times) of As and Br over livers of smelt, an important forage species. Concentrations of Cu and Br were enriched at least 10 times in lake trout livers compared to smelt livers.

A comparison of trace element concentrations between 1968 and 1972 suggests that environmental concentrations of Co and Cu did not change, but those of As and possibly Cd may have increased. However, these apparent increases over time could also be due to species-related differences in diet and habitat selection. Future studies will quantify the influence of species, life stage, diet, location, and season on trace element accumulation and transfer by fishes.

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DISSOLUTION OF THE SILICON FRUSTULES OF ASTERIONELLA FORMOSA AND FRAGILARIA CROTONENSIS AT 5 AND 15°C

H. L. Conway and J. Raupp*

Diatoms comprise approximately 70 to 90% of the total phytoplankton biomass produced during a seasonal cycle in Lake Michigan;[1,2] in fact, all the Great Lakes' phytoplankton communities may be dominated by diatoms.[3] These microscopic plants have an absolute requirement for silicon since it is used to build the cell well or frustule. The frustule is composed of polymerized silicic acid, $SiO_2 \cdot nH_2O$.

The processes of silicon uptake by the cell and dissolution of silicon from the frustule occur simultaneously in actively growing populations; however, the dissolution rate is only 6 to 20% of the maximal uptake rate.[4,5] After the diatom cell dies or is removed from the euphotic zone by sinking or grazing by herbivors, the energy-requiring process of silicon uptake ceases and frustule dissolution predominates. Recent studies have established that between 80 and 100% of the biologically active silicon in Lake Michigan is recycled each year.[6,7] Therefore, measuring the dissolution rates of important diatom species, at temperatures characteristic of surface and deep waters, is of primary importance in understanding and predicting silicon dynamics in the Great Lakes.

Unialgal populations of Asterionella formosa and Fragilaria crotonensis were grown in silicate-limited chemostats at a dilution rate of 0.02 h^{-1}.[8] After a steady state was attained, the two populations were removed from the chemostats, and each population was divided into two portions. Each portion was placed in a continuously-stirred, darkened flask at 5 or 15°C and sampled at varying intervals over a 2-1/2 month period. Reactive silicate and total cellular surface area were measured. No detectable increase in the reactive silicate concentration was observed in a control flask without diatom cells.

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Asterionella formosa populations exhibited dark uptake of silicate during the first 2 to 3 days of the experiment, after which time the silicate concentration began to increase in the flask (Figure 1). Fragilaria crotonensis populations reduced the silicate concentration to an undetectable level by the 13th day of the experiment, after which time the silicate concentration began to increase very slowly at 5°C and more rapidly at 15°C (Figure 1). The results summarized in Table 1 show the dissolution rate of A. formosa at 15°C was ~ 50 times faster than that observed for F. crotonensis at 5°C. Comparable dissolution rates were observed for A. formosa at 5°C and F. crotonensis at 15°C.

Qualitative aspects of the dissolution process can be seen in the scanning electron photomicrographs (Figures 2 and 3). The effect of dissolution on A. formosa cells at 15°C are (1) separation of the two halves (valves) of the frustule, and (2) reduction in the structural integrity of the cell wall. A collapse of the edges of the valve is shown in Figure 2c, as indicated by the arrow. For the A. formosa population at 5°C and F. crotonensis populations at 5°C and 15°C, the dissolution reduced the structural strength of the cell wall and the frustules began to fracture (Figures 2b, 3b 3c).

The results of this study show that (1) dissolution at 15°C is 5 (A. formosa) to 13 (F. crotonensis) times faster than at 5°C, and (2) at the same temperature, the dissolution rate of A. formosa frustules is 4 (15°C) to 9 (5°C) times faster than that observed for F. crotonensis.

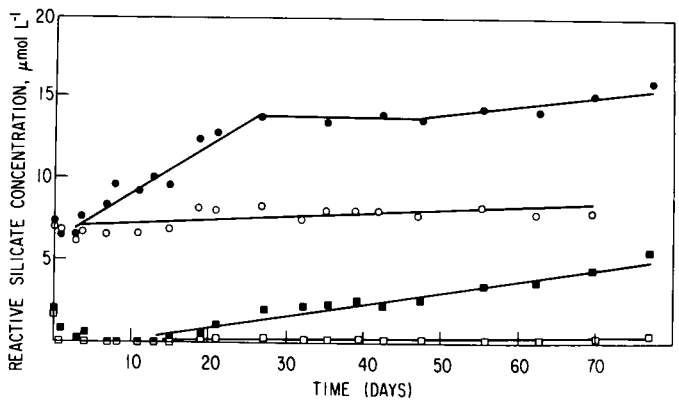

FIG. 1.--Reactive silicate concentration in the culture medium versus time. A. formosa o = 5°C, ● = 15°C; F. Crotonensis □= 5°C, ■ = 15°C. (ANL Neg. 149-78-115)

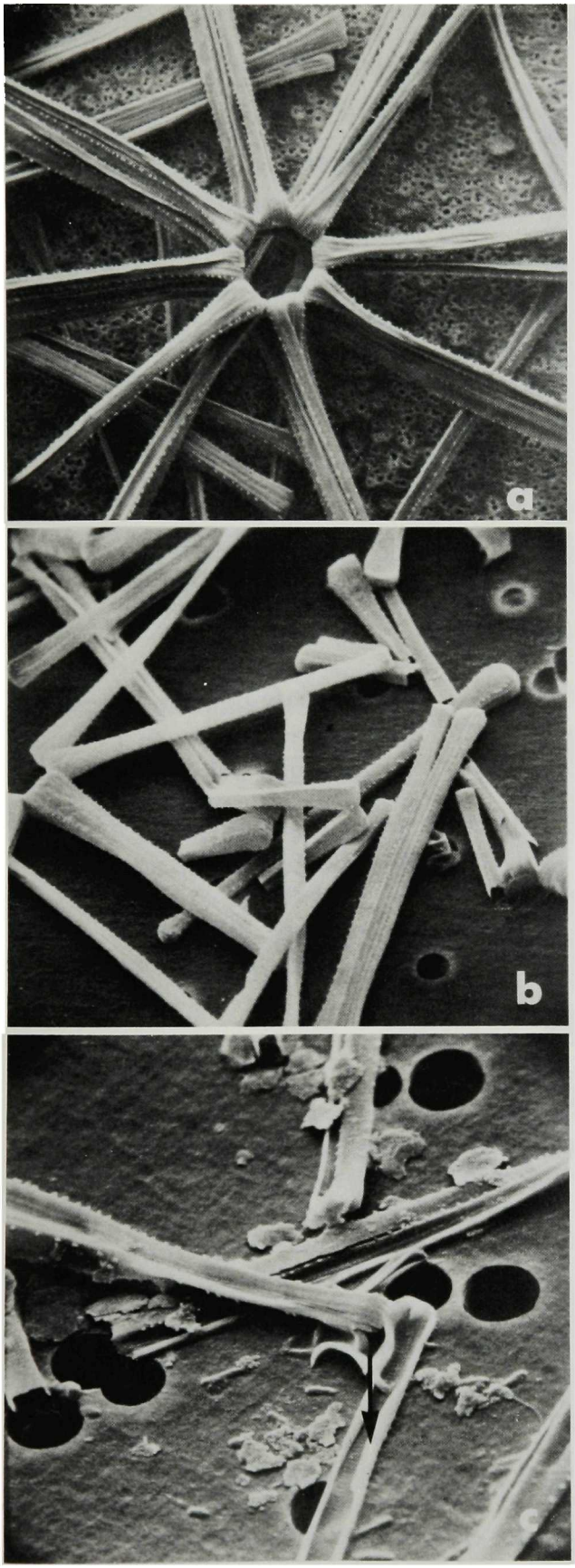

FIG. 2.--Scanning electron photomicrographs of A. formosa taken (a) at the start of the experiment (1500 ×), (b) at the end of the 5°C experiment (1500 ×), and (c) at the end of the 15°C experiment (3000 ×). The arrow (↓) in (c) is explained in the text.
(ANL Neg. 149-78-116).

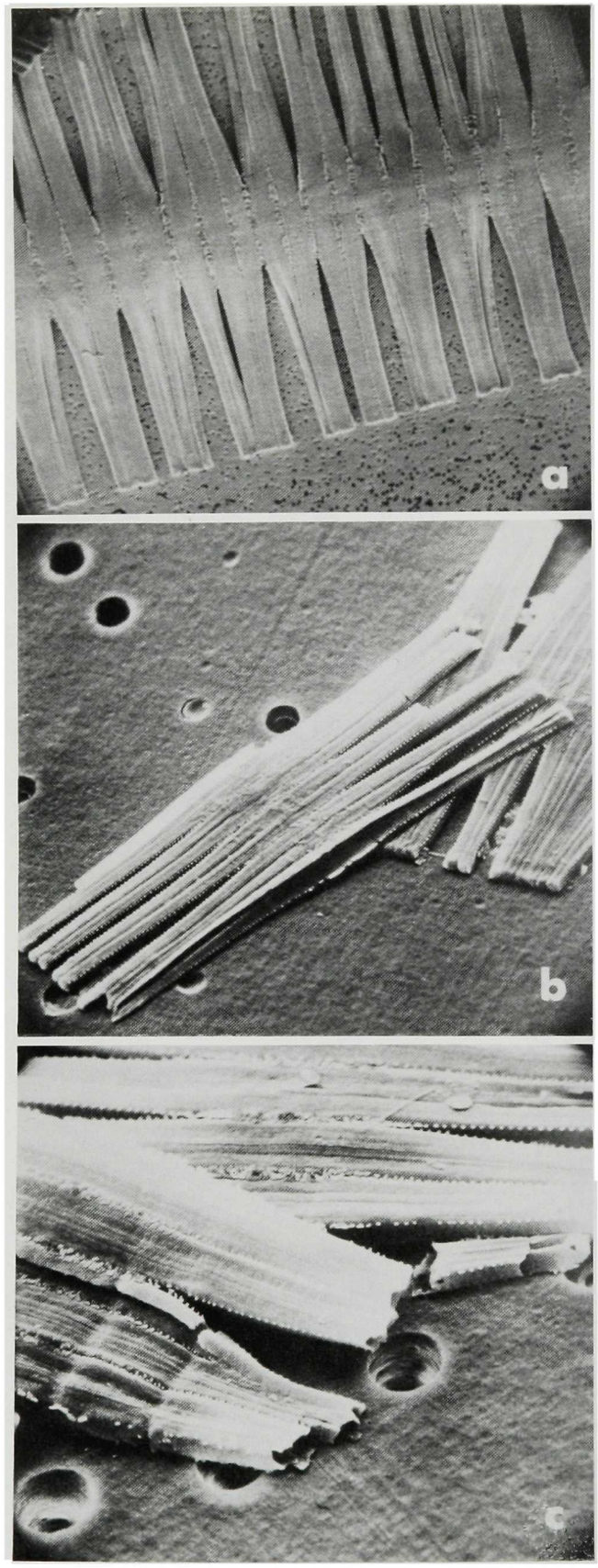

FIG. 3.--Scanning electron photomicrographs of F. crotonensis taken (a) at the start of the experiment (1500 ×), (b) at the end of the 5°C experiment (1500 ×), and (c) at the end of the 15°C experiment (3100 ×). (ANL Neg. 149-78-117)

In this study we have shown that dissolution is species and temperature dependent. This information, combined with the knowledge that sinking rate can also be species dependent,[9] may help explain the relative paucity of the frustules of important diatom species in the sediments of Lake Michigan.

Table 1. The dissolution rate of the silicon frustules of Asterionella formosa and Fragilaria crotonensis at 5 and 15°C.

Species	T°C	Dissolution rate,[a] pmol Si·mm^{-2}·d^{-1}
A. formosa	5	16
	15	87[b]
F. crotonensis	5	2
	15	23

[a]Derived from normalizing the slopes of the lines in Fig. 1 by cellular surface area of the population.

[b]Integrated mean value of the normalized slopes in Fig. 1.

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SORPTION AND DESORPTION OF CADMIUM BY ASTERIONELLA FORMOSA AND FRAGILARIA CROTONENSIS

H. L. Conway and S. C. Williams*

Cadmium has no known biological function in plants.[1] However, it is rapidly sorbed by phytoplankton,[2,3] resulting in decreased rates of growth and photosynthesis.[4,5] Previously, we determined that the time-dependent sorption of cadmium could be described by a hyperbolic function for the freshwater diatom, Asterionella formosa and Fragilaria crotonensis.[2] In the present study we examine the sorptive characteristics of cadmium in the light and in the dark for these two diatom species.

Unialgal populations that had previously been grown in silicate-limited, steady-state chemostats[6] at a dilution rate of 0.02 h^{-1} were used in the experiments. A subsample from each steady-state population was placed in one light bottle and in one dark bottle. Stable cadmium plus radioactive ^{115m}Cd was added to each 2-L bottle, yielding a final concentration of ~ 5 μg Cd L^{-1}. The cells were incubated under batch-culture conditions[7] for 24 hr and then resuspended in cadmium-free medium and incubated for an additional 52 hr. Samples were taken at discrete time intervals for radioactive counting and population cell volumes.

The initial rapid sorption of cadmium in the dark was comparable to that in the light (Figure 1). The cellular cadmium content of the light-grown A. formosa population, just prior to resuspending the cells in cadmium-free medium, was ~65% higher than that of the dark-grown A. formosa population; however, cellular cadmium content for both F. crotonensis populations was approximately the same. During the first 2 hr in cadmium-free medium, the cellular cadmium content decreased to ~45% of the value just prior to resuspension for A. formosa and ~28% for F. crotonensis. At the end of 52 hr in the cadmium-free medium

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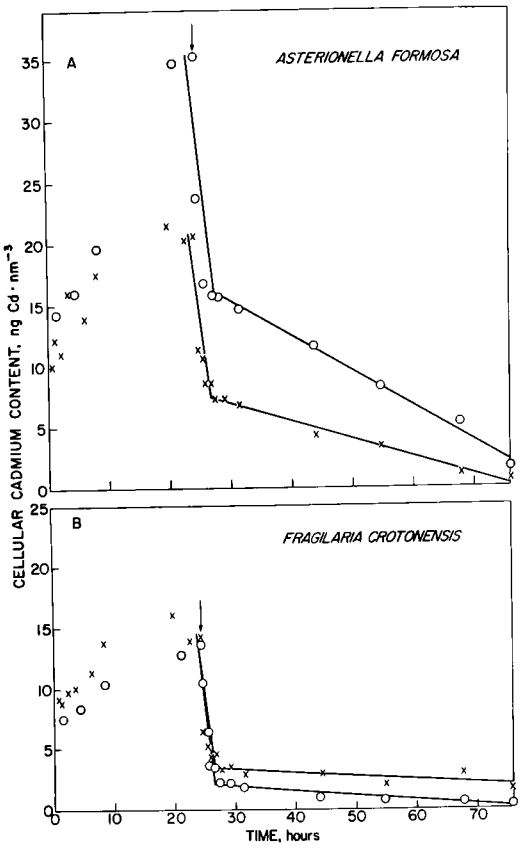

FIG. 1.--The cellular cadmium content versus time in light (O) and dar, (×). The arrow (↓) indicates the point at which the cells were resuspended in cadmium-free medium. The lines were fitted to the data points after the arrow (↓) for the first 2 hr and final 50 hr in cadmium-free medium.
(ANL Neg. 149-77-512 Rev. 1)

this percentage decreased to ~5% for both species. The slope of the straight line, fitted to the data points during the first 2 hr in cadmium-free medium, was similar for both species, ranging from -8 (A. formosa, light) to -4 (F. crotonensis, dark). However, after the initial rapid desorption the slope of the line decreased to -0.3 (light) and -0.1 (dark) for A. formosa and to -0.04 (light) and -0.03 (dark) for F. crotonensis.

Prior to the resuspension in cadmium-free medium, the ratio of cadmium sorption in the light to that in the dark was ~2 for A. formosa but only ~1 for F. crotonensis. This may be indicative of some cadmium being actively sorbed by A. formosa. The rapid desorption of cadmium, observed during the initial 2 hr in cadmium-free medium, indicates a "loosely-bound" fraction readily released by the cell. This fraction may be the cadmium adsorbed by the cell and if so indicates that a greater fraction of adsorbed cadmium is characteristic of F. crotonensis (~70%) than of A. formosa (~55%). After the initial desorption the rate decreased 10 to 100 times. The cadmium desorbed after

the first 2 hr may have been cadmium excreted from the cell contents. Sorption and desorption may occur simultaneously, in which case the desorption could only be observed when the sorption process was stopped. The residual cellular cadmium at the end of the experiment, ~ 2 ng Cd$\cdot(mm^3)^{-1}$, has also been observed as a constant value at the end of ~ 2 months in cadmium-free medium (unpublished data) and may represent that portion irreversibly tied up in metalloenzymes and complexed with amino acids, peptides, and proteins. It is, therefore, conceivable that < 5% of the total cadmium sorbed by the cell is actively involved in the detrimental effects observed in the test populations.[4]

The results of this study indicate that phytoplankton may have mechanisms for the cellular removal of toxic elements. However, further experiments should be done to distinguish clearly between passive and active processes, such as physical desorption and cellular excretion.

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A STUDY OF THE DISTRIBUTION OF CRUSTACEAN ZOOPLANKTON DURING AUGUST IN THE OFFSHORE REGION OF THE SOUTHERN BASIN OF LAKE MICHIGAN

D. L. Mellinger

During 1975–1977, zooplankton samples were collected in the offshore region of the southern basin of Lake Michigan.[1] The crustacean zooplankton community includes most of the primary consumers of the limnetic zone. These organisms, therefore, compose an essential link in the transfer of energy and potentially toxic substances from the photyplankton to the fish component of the Lake Michigan ecosystem.

The purpose of this article is to describe the variation found between duplicate sets of samples collected consecutively at one station and to compare these variations with between-station variability. The calculated standing crop biomass of crustacean zooplankton in the 0 to 40 m portion of the offshore region for August 1976 will be compared with those for August 1975 and 1977.

Samples were taken at station 5 (water depth, 67 m) and station 6 (87 m), which are located 10 km and 24 km southwest of Grand Haven, Michigan. A sample series consisted of four collections taken at sequential depth intervals (0–10, 10–20, 20–40, > 40 m) with a 50 cm closing net of 80 μm mesh. Samples were preserved with a 4% formalin solution and counted with a Wild M-5 stereomicroscope and a chambered counting cell.[2] Two subsamples were routinely counted. If the combined total of animals from these two subsamples was less than 500, a third subsample was counted. Adult animals and immature cladocerans were identified to species while immature copepods were classified as calanoid copepodites, cyclopoid copepodites, and nauplii. The data presented in this article do not include nauplii.

The results of two duplicate sets of samples collected in August 1976 are presented in Table 1. In the 0 to 40 m region, the standard errors of the means for duplicate samples average 10%. The between-stations variability is reflected by the standard errors of the monthly means. These between-stations standard errors compare very closely to the standard errors for duplicate samples means. These data indicate that the horizontal distribution of crustacean

Table 1. Average numbers of crustacean zooplankton per liter, in duplicate sets of samples collected during August 1976 (mean ± 1 S.E.).

Depth interval, m	Station 5 67 m 19 August (n = 2)	Station 6 87 m 17 August (n = 2)	Monthly mean (n = 4)
0—10	31.8 ± 5.0 (16%)[a]	30.6 ± 3.1 (10%)[a]	31.2 ± 2.4 (8%)[a]
10—20	12.8 ± 2.3 (18%)	16.0 ± 1.0 (6%)	14.4 ± 1.4 (10%)
20—40	1.5 ± 0.1 (4%)	1.9 ± 0.1 (6%)	1.7 ± 0.1 (8%)
>40	1.8 ± 0.5 (30%)	2.1 ± 0.1 (4%)	2.0 ± 0.2 (12%)

[a]Standard error (S.E.) of mean expressed as a percentage of mean.

zooplankton within the described depth intervals was quite homogeneous during August 1976.

The average calculated standing crop biomass (g/m^2) of crustacean zooplankton in the 0 to 40 m region for August 1976 was 2.55 ± 3%. Means ± 1 S.E. for August 1975 and 1977 were 2.97 ± 8% and 3.48± 8%, respectively. These August averages for standing crops in the 0 to 40 m region for 1975—1977 are remarkably similar (coefficient of variation = 16%).

These data suggest that horizontal patchiness in the offshore crustacean zooplankton community is not a major sampling problem during the period of summer thermal stratification.

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THE EFFECT OF CADMIUM ON THE FEEDING PROCESS OF THE CALANOID COPEPOD, LIMNOCALANUS MACRURUS

D. L. Mellinger

Calanoid copepods represent more than 75% of the average annual standing crop biomass of crustacean zooplankton in the offshore region of Lake Michigan.[1] The offshore calanoid copepod community is a complex one, consisting of at least eight species. Since Limnocalanus macrurus is the largest of the major calanoid species, it is a very important herbivore in the Lake Michigan food web. During the period of summer stratification, L. macrurus resides in the hypolimnion while its distribution during the other months is quite uniform throughout the entire water column.

The purpose of this experiment was to determine whether the filtering rate of Limnocalanus macrurus would be demonstrably affected when subjected to a sublethal cadmium concentration. From the CEPEX project,[2] it is reported that marine copepods produced fewer than the expected number of fecal pellets in the presence of a sublethal concentration of copper and suggested that this implied lower feeding rates.

The copepods were collected by net southwest of Grand Haven, Michigan, and transported to ANL. A common Lake Michigan diatom, Asterionella formosa, grown in chemostats,[3] was used as food for maintaining the copepods as well as for the experiment. Thirty adult copepods were placed in each of six experimental bottles (300 mL, BOD) and randomly assigned to one of the following groups: diatoms with added cadmium, or diatoms without added cadmium. Four control bottles (without copepods) were also prepared; two containing diatoms without added cadmium and two containing diatoms with added cadmium. The bottles were slowly rotated (1–2 rpm) to facilitate uniform particle distribution. The experiment was conducted at 6°C, in darkness , except for the few minutes of daily sampling procedure. Cadmium, as $CdCl_2$, was introduced to produce a calculated concentration of 10 μg/L and ^{115m}Cd was added as a radiotracer. Filtering rates were calculated for six 24-hr periods from the differences in cell numbers (biovolume) in control bottles without copepods compared to

experimental bottles with copepods. Cell counts (biovolume) were obtained using a Coulter particle counter.

Although Asterionella formosa typically forms eight-cell colonies ($\sim 2000\ \mu m^3$), the experimental cultures also contained other sized colonies. Consequently, filtering rates were calculated from the biovolume in the 286 to 2145 μm^3 portion of the particle spectrum (Figure 1). The average filtering rate for the cadmium-stressed copepods (0.11 ± 0.03 mL/copepods/hr) was 76% lower than those of the controls (0.442 ± 0.1 mL/copepod/hr). The stock cultures of diatoms were prepared 24 hr before the feeding experiment began (day s) and kept in the dark for the duration of the experiment. The apparent effects of cadmium on Asterionella formosa were to retard the frequency of cell division and also reduce the biovolume produced (Figure 2). Although the density of cells in the cadmium-stressed culture was somewhat less than in the control culture, the size array was quite similar until day 4. After day 4, the lower filtering rates of the cadmium-stressed copepods may have been confounded

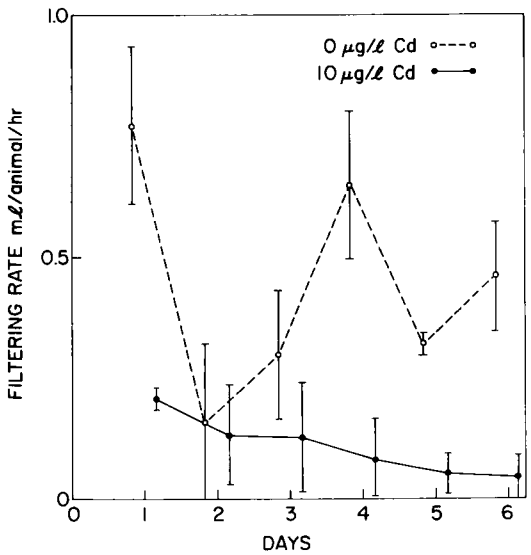

FIG. 1.--Filtering rates (mean ± 1 S.E.) of Limnocalanus macrurus for six 24-hr experimental periods (n = 3).
(ANL Neg. 149-77-335)

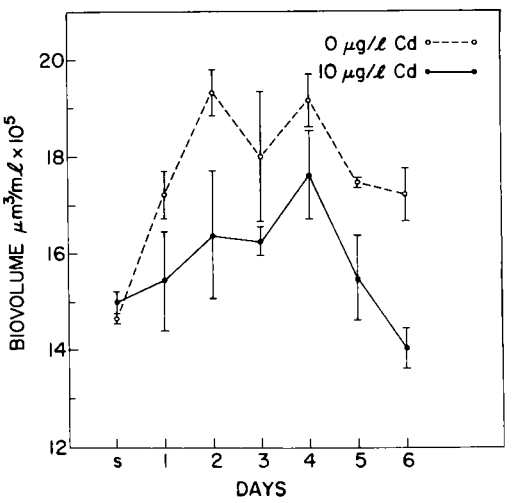

FIG 2.--Standing crop biomass (mean ± 1 S.E.) of Asterionella formosa in experimental bottles without copepods (n = 2).
(ANL Neg. 149-77-332)

by cadmium-induced changes in the density and size spectrum of the diatom culture.

In an attempt to evaluate the means by which cadmium is transferred from water to copepods, three groups of copepods were established and maintained for nine days under the same conditions as those described above except food (diatoms) was omitted. Five copepods were removed from each bottle on days 3, 6, and 9, and assayed for ^{115m}Cd burden. The concentration factors appear to increase in a linear manner over this time period (Figure 3).

The results of this pilot experiment indicate that a sublethal concentration of cadmium can significantly decrease the filtering rate of the calanoid copepod, Limnocalanus macrurus.

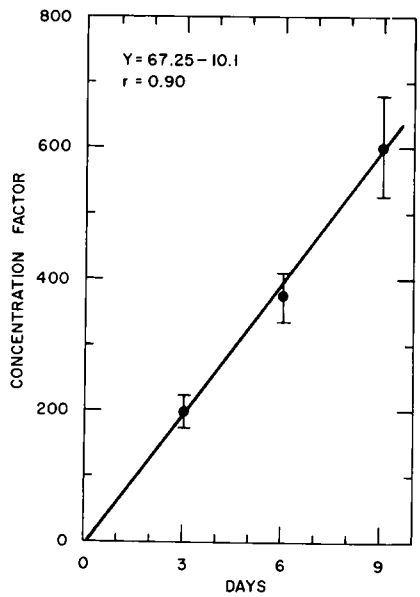

FIG. 3.--Concentration factors of ^{115m}Cd by Limnocalanus macrurus. (ANL Neg. 149-78-257)

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EFFECTS OF CADMIUM ENRICHMENT ON A LAKE MICHIGAN PLANKTON COMMUNITY

J. S. Marshall, D. L. Mellinger, and D. L. Saber*

In order to study the fate and effects of pollutants in aquatic ecosystems several multidisciplinary research programs have recently adopted experimental approaches employing whole lakes,[1,2] replicated ponds,[3] or large in situ enclosures of various kinds.[4–7] Large enclosures have been used mostly in small lakes or protected marine areas. In Lake Michigan, large plastic bags have been used in experiments lasting up to 2 weeks, but difficulties were encountered due to rigorous physical conditions.[8]

For experimental studies of energy-related pollutant effects in the Great Lakes, we developed and tested a new in situ technique employing polyethylene carboys as enclosures.[9] Our 1976 experiments in northern Green Bay, Lake Michigan, showed that cadmium enrichment > 5 μg Cd/L caused significant effects on several functional and structural attributes of the zooplankton community within 9 days, while the effects of enclosure (4–15 days) on the populations were mostly insignificant. This study indicated further that cadmium enrichment much lower than 5 μg/L would probably cause detectable effects on percentage similary (PS, an index related to beta diversity[10]) within 9 days and that in situ experiments longer than 15 days would be feasible.[9]

Therefore, in 1977 we conducted six 21-day experiments to determine the effects of cadmium enrichment in the 0 to 5 μg Cd/L range and its interaction with light (depth). The first four experiments covered the 0 to 5 μg Cd/L range, and the last two covered 0 to 1.6 μg Cd/L. The 1977 experiments were conducted in the same location in northern Green Bay, Lake Michigan, as those in 1976.[9] The results of the 1977 experiments are summarized in Table 1.

The effects of cadmium enrichment of 0 to 5 μg Cd/L on average numbers (numerical density) of total microcrustacea ($\overline{N}$) in Experiments 1 to 4, as indicated

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Table 1. Average numbers of different crustacean zooplankton (per 10 L) in duplicate samples (mean ± standard error) in six in situ, cadmium-enrichment experiments using incubations under different light (depth) conditions in Green Bay, Lake Michigan, 1977. Dates shown for each experiment indicate duration of incubation.

Category	Unincubated initial samples (July 19)	EXPERIMENT ONE July 19—August 9									
		Samples incubated in translucent (light) enclosures					Samples incubated in opaque (dark) enclosures				
		0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L	0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L
Cladocera											
Holopedium gibberum	3 ± 2	0	0	0	0	0	0	0	0	0	0
Bosmina longirostris	500 ± 88	2 ± 0	4	36 ± 13	39 ± 33	5 ± 2	2 ± 1	7 ± 1	9 ± 3	25	12 ± 7
Eubosmina coregoni	85 ± 30	20 ± 11	0	1 ± 1	2 ± 2	0	1 ± 1	5 ± 1	2 ± 2	0	0
Daphnia retrocurva	24 ± 2	2 ± 2	0	2 ± 2	4 ± 4	1 ± 1	0	0	0	0	0
D. galeata mendotae	12 ± 1	13 ± 6	11	13 ± 7	15 ± 9	14 ± 2	3 ± 1	2 ± 0	10 ± 1	59	31 ± 6
D. longiremis	8 ± 2	0	0	1 ± 1	0	0	0	0	0	0	0
Ceriodaphnia lacustris	9 ± 2	18 ± 10	0	9 ± 6	5 ± 5	1 ± 1	5 ± 2	11 ± 4	4 ± 4	8	5 ± 0
Chydorus sphaericus	92 ± 8	232 ± 98	168	84 ± 62	88 ± 13	24 ± 2	212 ± 28	126 ± 30	131 ± 1	120	24 ± 4
Copepoda: Cyclopoida											
Cyclops vernalis	4 ± 0	18 ± 1	8	13 ± 2	22 ± 9	9 ± 4	4 ± 2	3 ± 1	2 ± 2	2	3 ± 1
C. bicuspidatus thomasi	1 ± 0	9 ± 2	8	7 ± 3	0	0	27 ± 2	16 ± 3	16 ± 5	19	4 ± 2
Mesocyclops edax	2 ± 1	12 ± 4	11	9 ± 2	3 ± 3	8 ± 2	2 ± 2	1 ± 0	0	0	1 ± 1
Tropocyclops prasinus	5 ± 1	1 ± 1	1	2 ± 2	3 ± 3	1 ± 1	0	1 ± 1	0	0	0
Copepodites I-V	104 ± 6	18 ± 4	5	20 ± 1	25 ± 8	25 ± 5	16 ± 7	15 ± 0	20 ± 4	9	12 ± 9
Copepoda: Calanoida											
Eurytemora affinis	0	0	1	0	0	0	0	0	0	0	0
Diaptomus spp.	0	1 ± 1	1	3 ± 1	0	0	1 ± 1	0	1 ± 0	1	0
Copepodites I-V	19 ± 1	2 ± 2	1	1 ± 1	0	0	6 ± 2	1 ± 1	2 ± 2	0	1 ± 0

Category	Unincubated initial samples (July 20)	EXPERIMENT TWO July 20—August 9									
		Samples incubated in translucent (light) enclosures					Samples incubated in opaque (dark) enclosures				
		0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L	0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L
Cladocera											
Holopedium gibberum	8 ± 0	0	0	0	0	0	0	0	0	0	0
Bosmina longirostris	660 ± 154	8 ± 2	38 ± 17	55 ± 22	24 ± 10	1 ± 1	4 ± 1	0	7 ± 6	4	3 ± 1
Eubosmina coregoni	102 ± 16	38 ± 25	1 ± 1	1 ± 1	0	0	0	0	0	0	0
Daphnia retrocurva	32 ± 5	0	0	1 ± 1	1 ± 1	0	0	0	0	0	0
D. galeata mendotae	10 ± 1	39 ± 28	6 ± 3	31 ± 1	24 ± 6	1 ± 1	9 ± 2	18	12 ± 6	24	23 ± 11
D. longiremis	11 ± 4	0	0	0	0	0	0	0	0	0	0
Ceriodaphnia lacustris	19 ± 1	130 ± 91	38 ± 6	42 ± 15	18 ± 5	1 ± 1	9 ± 3	2	3 ± 1	1	7 ± 6
Chydorus sphaericus	105 ± 11	460 ± 125	301 ± 89	318 ± 156	104 ± 21	17 ± 3	179 ± 86	112	82 ± 24	18	9 ± 3
Copepoda: Cyclopoida											
Cyclops vernalis	3 ± 3	33 ± 1	32 ± 2	38 ± 8	24 ± 1	27 ± 8	1 ± 1	8	5 ± 0	6	4 ± 0
C. bicuspidatus thomasi	2 ± 1	4 ± 2	2 ± 2	6 ± 1	10 ± 5	1 ± 0	14 ± 6	9	12 ± 3	6	6 ± 2
Mesocyclops edax	2 ± 1	6 ± 1	4 ± 0	6 ± 4	4 ± 2	6 ± 1	1 ± 1	0	1 ± 1	0	1 ± 1
Tropocyclops prasinus	6 ± 1	0	1 ± 0	2 ± 1	0	1 ± 1	1 ± 1	0	1 ± 1	0	0
Copepodites I-V	80 ± 5	16 ± 6	23 ± 2	29 ± 14	17 ± 1	8 ± 1	7 ± 2	8	11 ± 1	12	8 ± 3
Copepoda: Calanoida											
Eurytemora affinis	0	1 ± 0	1 ± 1	1 ± 0	0	0	0	0	3 ± 3	0	0
Diaptomus spp.	0	4 ± 0	1 ± 1	0	0	1 ± 1	2 ± 2	0	0	0	0
Copepodites I-V	15 ± 1	5 ± 0	3 ± 1	3 ± 2	2 ± 1	0	1 ± 1	1	0	0	1 ± 1

Table 1. Continued.

Category	Unincubated initial samples (August 10)	EXPERIMENT THREE August 10—30									
		Samples incubated in translucent enclosures at 3—5 m depth					Samples incubated in translucent enclosures at 6—8 m depth				
		0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L	0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L
Cladocera											
Holopedium gibberum	9 ± 1	89 ± 19	1 ± 1	0	0	0	11 ± 6	0	0	0	0
Bosmina longirostris	252 ± 36	190 ± 28	458 ± 22	396 ± 45	136 ± 54	5 ± 4	104 ± 29	226 ± 14	174 ± 55	68 ± 39	11
Eubosmina coregoni	85 ± 11	140 ± 29	4 ± 1	1 ± 1	2 ± 1	4 ± 1	96 ± 4	4 ± 1	2 ± 2	1 ± 1	1
Daphnia retrocurva	144 ± 12	185 ± 28	259 ± 44	266 ± 14	366 ± 128	14 ± 8	19 ± 2	64 ± 2	71 ± 21	88 ± 22	25
D. galeata mendotae	9 ± 2	59 ± 2	59 ± 21	46 ± 6	59 ± 26	26 ± 14	59 ± 4	24 ± 6	42 ± 10	42 ± 21	52
D. longiremis	46 ± 11	34 ± 1	37 ± 3	22 ± 5	8 ± 1	0	2 ± 2	10 ± 5	12 ± 6	4 ± 1	0
Ceriodaphnia lacustris	116 ± 18	14 ± 3	12 ± 9	20 ± 2	7 ± 3	1 ± 1	2 ± 1	12 ± 2	8 ± 1	18 ± 2	15
Chydorus sphaericus	88 ± 19	666 ± 214	575 ± 158	465 ± 78	231 ± 29	41 ± 24	381 ± 70	782 ± 9	330 ± 34	218 ± 24	94
Copepoda: Cyclopoida											
Cyclops vernalis	6 ± 1	33 ± 1	31 ± 2	29 ± 1	24 ± 4	26 ± 1	24 ± 8	24 ± 4	25 ± 6	22 ± 2	12
C. bicuspidatus thomasi	18 ± 1	43 ± 1	30 ± 2	35 ± 5	39 ± 8	11 ± 1	28 ± 6	15 ± 1	16 ± 5	14 ± 1	15
Mesocyclops edax	1 ± 1	16 ± 4	15 ± 0	14 ± 4	15 ± 2	10 ± 2	14 ± 2	8 ± 2	12 ± 1	10 ± 2	10
Tropocyclops prasinus	37 ± 1	62 ± 9	62 ± 12	52 ± 5	72 ± 20	42 ± 4	25 ± 10	22 ± 14	19 ± 2	20 ± 5	8
Copepodites I-V	161 ± 70	55 ± 4	62 ± 5	54 ± 0	50 ± 19	48 ± 3	45 ± 2	52 ± 2	52 ± 8	68 ± 9	34
Copepoda: Calanoida											
Eurytemora affinis	0	9 ± 1	8 ± 1	11 ± 1	9 ± 2	2 ± 1	6 ± 4	9 ± 4	3 ± 1	8 ± 5	9
Diaptomus spp.	1 ± 1	4 ± 1	3 ± 2	2 ± 1	5 ± 0	1 ± 1	2 ± 1	1 ± 1	6 ± 1	2 ± 0	2
Copepodites I-V	9 ± 0	6 ± 1	7 ± 1	7 ± 1	6 ± 3	2 ± 2	5 ± 2	4 ± 1	6 ± 4	4 ± 1	1

Category	Unincubated initial samples (August 10)	EXPERIMENT FOUR August 10—30									
		Samples incubated in translucent enclosures at 3—5 m depth					Samples incubated in translucent enclosures at 6—8 m depth				
		0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L	0 μg Cd/L	0.63 μg Cd/L	1.25 μg Cd/L	2.5 μg Cd/L	5.0 μg Cd/L
Cladocera											
Holopedium gibberum	14 ± 2	142 ± 18	0	2 ± 2	0	0	0	0	0	0	0
Bosmina longirostris	296 ± 21	114 ± 4	472 ± 99	365 ± 24	222 ± 60	15 ± 11	35 ± 10	129 ± 41	181 ± 9	35 ± 2	26 ± 19
Eubosmina coregoni	124 ± 15	258 ± 96	6 ± 4	11 ± 10	1 ± 1	8 ± 5	62 ± 11	1 ± 1	5 ± 5	3 ± 3	0
Daphnia retrocurva	128 ± 6	174 ± 22	222 ± 99	326 ± 225	444 ± 138	64 ± 38	52 ± 5	102 ± 66	149 ± 12	69 ± 38	22 ± 11
D. galeata mendotae	3 ± 3	64 ± 14	99 ± 15	80 ± 28	229 ± 78	90 ± 64	18 ± 8	28 ± 2	36 ± 9	34 ± 14	25 ± 10
D. longiremis	30 ± 6	6 ± 2	12 ± 8	8 ± 4	3 ± 1	1 ± 1	1 ± 1	1 ± 1	2 ± 1	1 ± 1	0
Ceriodaphnia lacustris	132 ± 8	5 ± 4	15 ± 15	4 ± 2	2 ± 1	8 ± 5	1 ± 1	4 ± 4	7 ± 1	1 ± 1	2 ± 2
Chydorus sphaericus	166 ± 12	346 ± 25	469 ± 61	300 ± 186	342 ± 5	131 ± 69	408 ± 117	474 ± 28	449 ± 14	366 ± 5	89 ± 19
Copepoda: Cyclopoida											
Cyclops vernalis	6 ± 1	40 ± 16	56 ± 5	44 ± 4	42 ± 1	40 ± 4	40 ± 2	45 ± 9	44 ± 5	44 ± 2	30 ± 5
C. bicuspidatus thomasi	6 ± 1	26 ± 4	15 ± 1	20 ± 9	15 ± 9	4 ± 1	8 ± 1	9 ± 2	5 ± 0	4 ± 1	4 ± 2
Mesocyclops edax	1 ± 0	19 ± 1	16 ± 4	16 ± 4	18 ± 0	16 ± 1	14 ± 1	11 ± 1	12 ± 6	9 ± 1	6 ± 2
Tropocyclops prasinus	29 ± 8	41 ± 6	59 ± 5	51 ± 2	58 ± 6	52 ± 2	38 ± 4	16 ± 4	12 ± 2	34 ± 6	5 ± 2
Copepodites I-V	218 ± 21	69 ± 19	68 ± 5	60 ± 6	40 ± 1	35 ± 6	40 ± 0	39 ± 5	35 ± 2	39 ± 14	30 ± 2
Copepoda: Calanoida											
Eurytemora affinis	0	11 ± 0	12 ± 4	19 ± 6	11 ± 4	9 ± 4	4 ± 1	9 ± 0	10 ± 4	15 ± 1	5 ± 2
Diaptomus spp.	2 ± 1	4 ± 4	2 ± 0	4 ± 1	6 ± 1	1 ± 1	1 ± 1	3 ± 1	1 ± 1	0	1 ± 1
Copepodites I-V	14 ± 5	10 ± 0	12 ± 4	8 ± 1	4 ± 1	0	8 ± 0	8 ± 1	2 ± 1	2 ± 2	1 ± 1

Table 1. Continued

Category	Unincubated initial samples (August 31)	EXPERIMENT FIVE August 31—September 21									
		Samples incubated in translucent enclosures at 4—6 m depth					Samples incubated in translucent enclosures at 6—8 m depth				
		0 μg Cd/L	0.2 μg Cd/L	0.4 μg Cd/L	0.8 μg Cd/L	1.6 μg Cd/L	0 μg Cd/L	0.2 μg Cd/L	0.4 μg Cd/L	0.8 μg Cd/L	1.6 μg Cd/L
Cladocera											
Holopedium gibberum	20 ± 5	24 ± 16	16 ± 2	12 ± 2	23 ± 7	1 ± 1	8 ± 2	4 ± 0	4 ± 1	1 ± 1	1 ± 1
Bosmina longirostris	100 ± 1	68 ± 3	48 ± 45	84 ± 74	116 ± 42	92 ± 92	80 ± 25	56 ± 11	54 ± 12	41 ± 29	97 ± 58
Eubosmina coregoni	167 ± 4	82 ± 6	12 ± 8	13 ± 12	4 ± 0	1 ± 1	57 ± 8	11 ± 3	3 ± 1	1 ± 0	0
Daphnia retrocurva	65 ± 5	49 ± 17	51 ± 18	70 ± 2	61 ± 11	98 ± 72	65 ± 26	35 ± 9	40 ± 9	53 ± 6	93 ± 64
D. galeata mendotae	5 ± 3	38 ± 17	21 ± 2	24 ± 5	34 ± 6	99 ± 12	36 ± 6	30 ± 8	44 ± 3	32 ± 11	25 ± 5
D. longiremis	24 ± 0	29 ± 7	37 ± 16	52 ± 14	59 ± 31	25 ± 9	14 ± 1	16 ± 5	26 ± 13	12 ± 4	19 ± 14
Ceriodaphnia lacustris	53 ± 2	26 ± 8	9 ± 8	14 ± 6	18 ± 10	11 ± 11	11 ± 2	20 ± 12	4 ± 0	7 ± 3	9 ± 6
Chydorus sphaericus	73 ± 9	218 ± 9	137 ± 8	314 ± 169	148 ± 57	153 ± 8	154 ± 2	184 ± 18	130 ± 4	138 ± 39	124 ± 56
Copepoda: Cyclopoida											
Cyclops vernalis	5 ± 2	16 ± 1	14 ± 0	20 ± 2	16 ± 5	13 ± 6	16 ± 1	16 ± 1	14 ± 2	12 ± 2	12 ± 1
C. bicuspidatus thomasi	9 ± 5	72 ± 3	70 ± 9	58 ± 6	57 ± 12	48 ± 16	54 ± 9	38 ± 1	27 ± 4	37 ± 14	38 ± 3
Mesocyclops edax	4 ± 0	18 ± 1	12 ± 6	11 ± 0	9 ± 2	18 ± 4	10 ± 1	9 ± 6	9 ± 2	11 ± 1	5 ± 1
Tropocyclops prasinus	31 ± 3	28 ± 5	34 ± 6	26 ± 6	27 ± 6	21 ± 4	21 ± 2	22 ± 8	18 ± 2	24 ± 18	22 ± 6
Copepodites I-V	389 ± 5	77 ± 11	78 ± 2	70 ± 10	72 ± 4	62 ± 6	64 ± 1	75 ± 1	71 ± 8	94 ± 13	101 ± 9
Copepoda: Calanoida											
Eurytemora affinis	2 ± 1	1 ± 1	3 ± 3	1 ± 1	3 ± 3	2 ± 1	0	0	6 ± 4	3 ± 2	3 ± 1
Diaptomus spp.	6 ± 1	7 ± 1	10 ± 2	6 ± 1	8 ± 1	8 ± 4	6 ± 1	9 ± 2	6 ± 2	7 ± 1	9 ± 1
Copepodites I-V	15 ± 4	5 ± 1	6 ± 4	7 ± 1	6 ± 1	6 ± 1	11 ± 1	7 ± 1	9 ± 3	9 ± 1	12 ± 2

Category	Unincubated initial samples (Sept. 1)	EXPERIMENT SIX September 1—21									
		Samples incubated in translucent enclosures at 4—6 m depth					Samples incubated in translucent enclosures at 6—8 m depth				
		0 μg Cd/L	0.2 μg Cd/L	0.4 μg Cd/L	0.8 μg Cd/L	1.6 μg Cd/L	0 μg Cd/L	0.2 μg Cd/L	0.4 μg Cd/L	0.8 μg Cd/L	1.6 μg Cd/L
Cladocera											
Holopedium gibberum	38 ± 8	21 ± 9	16 ± 9	27 ± 8	0	2 ± 2	16 ± 8	6 ± 5	16 ± 14	2 ± 1	1 ± 0
Bosmina longirostris	184 ± 11	8 ± 2	82 ± 79	106 ± 28	83 ± 62	108 ± 67	30 ± 22	39 ± 19	41 ± 17	67 ± 22	64 ± 45
Eubosmina coregoni	279 ± 18	61 ± 11	39 ± 26	30 ± 12	6 ± 1	4 ± 0	64 ± 30	22 ± 2	16 ± 14	2 ± 1	3 ± 3
Daphnia retrocurva	214 ± 9	35 ± 10	20 ± 5	24 ± 3	30 ± 12	38 ± 2	16 ± 9	14 ± 9	21 ± 12	24 ± 4	16 ± 14
D. galeata mendotae	16 ± 2	71 ± 12	56 ± 18	63 ± 3	47 ± 27	35 ± 4	34 ± 1	40 ± 4	40 ± 5	29 ± 3	29 ± 12
D. longiremis	38 ± 1	12 ± 2	25 ± 15	22 ± 1	11 ± 2	21 ± 10	1 ± 1	8 ± 2	24 ± 14	28 ± 13	4 ± 2
Ceriodaphnia lacustris	76 ± 6	6 ± 2	8 ± 5	8 ± 8	6 ± 1	4 ± 1	28 ± 2	14 ± 8	9 ± 6	5 ± 1	4 ± 2
Chydorus sphaericus	89 ± 5	414 ± 236	500 ± 178	216 ± 26	189 ± 21	244 ± 117	269 ± 4	234 ± 89	156 ± 36	144 ± 42	157 ± 53
Copepoda: Cyclopoida											
Cyclops vernalis	8 ± 4	25 ± 4	34 ± 0	18 ± 1	19 ± 2	22 ± 1	27 ± 1	20 ± 0	23 ± 4	18 ± 4	22 ± 2
C. bicuspidatus thomasi	32 ± 0	69 ± 2	74 ± 14	62 ± 11	46 ± 4	42 ± 3	58 ± 19	53 ± 8	47 ± 11	48 ± 2	46 ± 19
Mesocyclops edax	12 ± 4	18 ± 2	12 ± 3	18 ± 1	18 ± 2	15 ± 2	19 ± 6	18 ± 1	14 ± 1	24 ± 5	19 ± 7
Tropocyclops prasinus	34 ± 2	16 ± 6	11 ± 1	21 ± 3	18 ± 3	18 ± 3	13 ± 1	12 ± 2	11 ± 1	12 ± 4	21 ± 7
Copepodites I-V	399 ± 25	105 ± 12	109 ± 1	88 ± 30	91 ± 14	128 ± 42	71 ± 5	85 ± 16	76 ± 10	92 ± 9	92 ± 5
Copepoda: Calanoida											
Eurytemora affinis	2 ± 1	1 ± 1	0	0	6 ± 1	6 ± 4	0	3 ± 3	3 ± 1	4 ± 2	1 ± 1
Diaptomus spp.	15 ± 1	4 ± 1	6 ± 1	6 ± 1	13 ± 4	8 ± 1	5 ± 2	8 ± 1	6 ± 1	6 ± 1	7 ± 2
Copepodites I-V	15 ± 1	12 ± 1	8 ± 1	9 ± 2	6 ± 3	6 ± 1	10 ± 2	4 ± 3	11 ± 2	9 ± 2	10 ± 6

by the slopes of linear regressions of $\overline{N}$ on cadmium, were greater in "light" than in "dark" or in 3 to 5 m compared with 6 to 8 m incubations, and t-tests showed that the differences between these slopes were significant ($p < 0.05$) in Experiments 2 and 3. Measurements of dissolved oxygen concentrations suggest that this synergistic interaction with light (depth) was an indirect effect of cadmium due to reduction of photosynthesis. Total numbers of microcrustacea and alpha diversity, as indicated by average values of Hill's numbers[11] were not significantly affected within 3 weeks by < 1.6 μg Cd/L, whereas percentage similarity was reduced by an enrichment as small as 0.2 μg Cd/L, the lowest concentration tested. Percentage similarity decreased linearly with added cadmium (in the 0 to 5 μg Cd/L range) in the Lake Michigan experiments, and the results from an experiment in Canada's ELA Lake 223[12] for day 24 fall close to a linear regression of PS on cadmium (not shown) based on the six 21-day Lake Michigan experiments.

Enclosure effects were assessed from measurements of percentage similarity and coefficient of community[10] for the control enclosures (relative to the lake community's average composition) and for the lake samples (relative to the same average) on the same date. Enclosure effects on specific categories of microcrustacea were assessed from differences in their average abundances in the control enclosures after incubations and the lake on the same date. Enclosure effects on specific categories of microcrustacea were assessed from differences in their average abundances in the control enclosures after incubations and the lake on the same date. Enclosure in opaque (amber) polyethylene carboys or in translucent carboys at depths > 8 m caused large reductions of both percentage similarity and coefficient of community. Enclosure in translucent carboys at < 8 m resulted in smaller reductions, and the effects of enclosure at 3 to 5 m were smaller than at 6 to 8 m. The largest significant differences in average abundance of specific categories of microcrustacea were due to increases in Chydorus sphaericus and decreased in cyclopoid copepodites I-V. The results indicate that the effects of enclosure in translucent polyethylene carboys at optimal depths for up to 3 weeks are probably not much greater than those in larger enclosures of various kinds.

The results of this study indicate further that cadmium enrichment as low as 0.05 to 0.1 μg Cd/L would probably cause detectable reductions of percentage similarity within 3 weeks and that experiments longer than 3 weeks are feasible at optimal incubation depths. Additional intercomparisons with ELA experiments employing large enclosures, isolated bays or whole lakes are needed, however, to determine the applicability of shorter term experiments using small enclosures in the Great Lakes.

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ZOOPLANKTON RESPONSES TO CADMIUM ENRICHMENT IN LARGE ENCLOSURES IN CANADA'S EXPERIMENTAL LAKES AREA LAKE 223

J. S. Marshall and D. L. Mellinger

Canada's Experimental Lakes Area (ELA), containing 45 lakes in northwestern Ontario, was established by the government of Canada in 1966 for experimental studies of eutrophication effects in whole-lake systems.[1] Toxic substances as well as nutrients usually enter lakes subject to cultural stress, so it was recognized that the effects and interactions of toxic substances should also be studied.[1] Because of our in situ studies of cadmium toxicity to Lake Michigan zooplankton using small enclosures and the difficulty of using large enclosures in the Great Lakes,[2] we were most grateful for an opportunity to participate in a multidisciplinary experimental study of ecosystem responses to cadmium enrichment using five large enclosures in ELA Lake 223. The purpose of this report is to summarize the analyses of the zooplankton samples and to present preliminary interpretations.

Lake 223 is an oligotrophic, soft-water lake containing zooplankton common to the Great Lakes as well as to other smaller lakes in Ontario.[3] The five enclosures used in this study consisted of nylon-reinforced polyethylene cylinders, 10 m in diameter, extending from the surface to the bottom of the lake at a depth of approximately two meters. Each cylinder was supported at the surface by a ring of wood-reinforced Styrofoam floats and secured to the bottom by weights. On 4 July 1977, $CdCl_2$ was added to four of the five enclosures to produce calculated initial concentrations of 1, 3, 10, and 30 μg Cd/L, leaving one enclosure as a control. Tritiated water (HTO) and ^{115m}Cd were also added as radiotracers for water balance and cadmium uptake studies. After 4 July samples of water, plankton, benthos, and fish were collected routinely for radioactive and/or stable cadmium analyses. Zooplankton samples were collected with a quadruple tow net (one pair with 73-μm apertures and another pair with 35-μm apertures) at approximately weekly intervals from 8 July until 17 August (day 44) and preserved in 4% formalin. Zooplankton identifications were made with the aid of keys, illustrations, and descriptions.[4,5]

Quantitative analyses were made of rotifers and nauplii in a Sedgewick-Rafter chamber and of other crustaceans in a chambered counting cell[6] using Wild M20 and M5 microscopes, respectively. The results are shown in Tables 1 and 2.

The numerical density of both crustaceans and rotifers in the enclosures enriched with 0 to 1 μg Cd/L became significantly greater than in those enriched to higher concentrations. The effect of cadmium on crustaceans became most pronounced on days 24 and 31 and then decreased, probably due to decreasing concentrations of cadmium remaining in the water. The depressing effect of cadmium on density of total crustaceans is numerically dominated by its effect on nauplii; however, the density of crustaceans excluding nauplii showed a similar depression. After day 10 the average density of crustaceans exclusive of nauplii in the enclosures to which 0 to 1 μg Cd/L had been added remained higher than that in the other three enclosures, and the difference was significant ($p < 0.05$) on days 17, 31, 38, and 44. The density of total rotifers in the enclosures to which 0 to 1 μg Cd/L had been added also remained higher than that in the other enclosures after day 10, although considerable recovery from depression was apparent on days 38 and 44 in the enclosure to which 3 μg Cd/L had been added. The lower density of rotifers in the control enclosure than in the enclosure to which 1 μg Cd/L had been added may be due to competition with the much denser populations of nauplii and other herbivorous crustaceans in the control enclosure.

The apparent effects of cadmium enrichment in the large enclosures in ELA Lake 223 tend to corroborate those observed in Lake Michigan experiments using much smaller enclosures. In the Lake Michigan experiments the density of crustaceans (exclusive of nauplii) and species diversity were not significantly affected within 21 days by additions of less than 1.6 μg Cd/L, whereas percentage similarity (PS) was reduced by as little as 0.2 μg Cd/L.[2] In the ELA Lake 223 experiment on day 24 PS values for the crustacean zooplankton communities in the enclosure to which 1 and 3 μg Cd/L had been added fall close to a linear regression for PS on cadmium for 21-day experiments in Lake Michigan using enrichments of 0 to 5 μg Cd/L.[2]

Table 1. Numbers of individuals (m^{-3}) of various categories of crustacean zooplankton on different dates in five large enclosures in ELA lake 223. Subheadings for each date are cadmium concentrations (μg/L) that were added to the enclosures on 4 July 1977 (day 0).

Category	8 VII 77 (day 4)					14 VII 77 (day 10)					21 VII 77 (day 17)					28 VII 77 (day 24)				
	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30
Cladocera																				
Bosmina longirostris	98	103	22	106	47	591	218	338	36	0	1315	569	92	75	24	3455	2228	584	40	85
Chydorus sphaericus	141	32	0	68	194	123	58	118	80	112	74	90	53	224	56	91	48	16	4	644
Copepoda: Cyclopoida																				
Tropocyclops prasinus	374	897	478	2417	357	1429	417	1265	1261	168	3356	535	397	1254	677	6439	1834	568	143	34
Mesocyclops edax	12	19	7	83	116	19	173	22	94	40	20	28	53	254	32	38	21	56	15	8
Copepodites I-V	2515	3353	544	2848	3550	1740	1891	515	696	760	1255	2104	397	276	218	8515	1772	520	125	331
Copepoda: Calanoida																				
Diaptomus minutus	172	417	51	758	310	71	71	191	87	40	101	125	137	149	40	136	62	400	33	17
Copepodites I-V	141	160	29	83	395	58	83	7	51	64	221	444	519	194	153	1182	648	440	77	119

Category	4 VIII 77 (day 31)					11 VIII 77 (day 38)					17 VIII 77 (day 44)					28 IX 77 (day 87)				
	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30
Cladocera																				
Bosmina longirostris	6842	2717	493	14	32	2929	6939	1352	41	296	6776	11310	3129	98	1373	717	4101	1047	2100	1968
Chydorus sphaericus	230	158	37	0	323	34	85	0	4	1674	207	122	38	19	4227	173	291	1757	371	390
Copepoda: Cyclopoida																				
Tropocyclops prasinus	3322	2586	515	133	56	2407	3486	906	260	240	1534	1731	639	117	322	277	1190	609	429	240
Mesocyclops edax	0	20	7	7	8	17	17	0	0	39	0	0	13	0	21	0	0	0	18	0
Copepodites I-V	11810	4849	1015	119	137	7088	4541	1391	576	691	3034	1958	805	532	1352	1712	5582	1757	1176	1429
Copepoda: Calanoida																				
Diaptomus minutus	197	86	184	42	8	236	238	407	126	60	34	0	204	34	43	16	25	101	0	19
Copepodites I-V	493	855	559	105	16	707	731	591	123	245	207	227	421	125	193	16	53	254	353	305

Table 2. Numbers of individuals per liter of copepod nauplii and planktonic rotifers on different dates in five large enclosures in ELA lake 223. Subheadings of each date are cadmium concentrations (μg/L) that were added to the enclosures on 4 July 1977 (day 0).

Category	8 VII 77 (day 4)					14 VII 77 (day 10)					21 VII 77 (day 17)					28 VII 77 (day 24)				
	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30
Copepoda																				
Copepod nauplii	22	18	65	52	12	22	35	16	9	1	48	12	17	7	5	214	10	10	6	9
Rotifera																				
Trichocerca cylindrica	0	6	3	2	3	4	10	9	0	0	12	58	8	1	1	126	246	42	0	2
Keratella taurocephala	16	25	30	38	2	14	50	28	13	3	37	58	32	4	2	125	138	29	2	5
Keratella cochlearis	0	0	0	2	0	0	0	2	1	0	0	2	0	0	0	0	6	6	0	0
Kellicottia longispina	20	7	3	5	17	6	3	3	0	3	2	0	4	1	1	1	6	0	0	0
Conochilus unicornis	128	99	205	72	8	44	68	26	62	0	29	165	96	35	5	0	208	115	2	11
Ploesoma sp.	18	9	30	4	6	25	9	7	12	0	20	13	6	9	2	25	17	6	0	2
Polyarthra spp. (2)	18	45	112	98	35	21	175	112	98	11	13	410	277	124	42	292	677	127	88	95
Others	0	4	17	10	8	0	3	9	3	0	0	4	4	4	1	4	4	4	1	2

Category	4 VIII 77 (day 31)					11 VIII 77 (day 38)					17 VIII 77 (day 44)					28 IX 77 (day 87)				
	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30	0	1	3	10	30
Copepoda																				
Copepod nauplii	256	50	20	4	17	91	68	17	6	11	100	89	14	1	24					
Rotifera																				
Trichocerca cylindrica	200	192	49	1	0	148	43	152	11	2	38	4	288	15	5					
Keratella taurocephala	210	490	54	1	14	381	888	115	16	25	516	733	211	15	31					
Keratella cochlearis	0	54	20	1	0	0	152	155	5	0	0	154	415	20	1					
Kellicottia longispina	0	0	0	0	0	0	0	4	1	0	2	0	0	1	0					
Conochilus unicornis	2	86	45	21	31	7	21	38	18	32	67	25	80	24	33					
Ploesoma sp.	12	12	0	0	5	6	10	4	1	4	5	13	9	0	1					
Polyarthra spp. (2)	156	1400	106	65	203	88	1023	315	164	122	52	854	493	125	127					
Others	5	12	7	8	2	4	18	0	5	0	8	13	6	4	0					

The results of this study tend to verify those of our experiments in Lake Michigan using much smaller enclosures—at least up to 3 weeks. Additional intercomparisons are needed, however, to assess fully the usefulness of small enclosures for in situ studies of energy-related stresses in the Great Lakes.

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REACTIONS OF CADMIUM IN LAKE MICHIGAN: KINETICS AND EQUILIBRIA*

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Considerable research has been conducted to determine the concentrations of trace metals in the Great Lakes and to ascertain their sources. Investigations have also been conducted to establish the fate and effect of trace metals on aquatic organisms. We examined the chemical and physical reactions of cadmium with colloidal and soluble fractions present in Lake Michigan waters to attain a greater understanding of processes which may control both the fate and effects of cadmium in aquatic systems. For the complex formation processes studied, the equilibrium constant, complex formation capacity and reaction kinetics were determined.

Lake Michigan water samples were collected both at the shore near Chicago and approximately 20 miles offshore and were filtered through 0.45 μm membrane filters. A portion of the filtrate was passed through a Biorad ultrafilter having a molecular weight cutoff of approximately 30,000 to separate soluble and colloidal matter.

Capacities for formation of complexes and stability constants for the soluble (ultrafiltrate) and soluble colloidal (0.45 μm filtrate) fractions were determined by the anodic stripping voltametric (ASV) method described by Shuman and Woodward.[1] The lake water samples were first purged of oxygen using a N_2-CO_2 gas mixture which also maintained the sample at constant pH. The samples were titrated with cadmium, and after a 10 min equilibration period, the electroactive cadmium was determined by differential pulse ASV. Complex formation capacity, the point at which the metal reactive sites are saturated, was determined by noting the inflection point of the titration curves. Because

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anodic stripping voltametry does not respond to all forms of metal, the sensitivity is reduced in the presence of ligands forming strong complexes. The slopes of the titration curve before and after the point at which complex forming capacity was exceeded and the value of the complex forming capacity were used to determine the conditional stability constant for the complex.[1]

No short-term complex formation with cadmium was found with material in the ultrafiltrate (soluble fraction). There was considerable short-term complex formation of cadmium with material which was not retained by the 0.45 μm membrane filter (soluble plus colloidal fraction). What is more, both complex forming capacity and the stability constant were similar for the membrane filtered samples. The complex forming capacities were 4.2×10^{-8} M (offshore) and 2.8×10^{-8} M (at shore) and the stability constants were 8.2×10^{7} (offshore) and 12.0×10^{7} (at shore). Thus, for an addition of 50 μg Cd/L, which would more than double the existing concentration, it is predicted that approximately three-quarters of the added metal would be taken up in a complex within the 10 min reaction period. For an addition of even 1 μg Cd/L, over two-thirds would be complexed. The completeness of the reaction was tested by conducting a series of three analyses conducted over the first 13 min after cadmium addition. The reaction was complete within 2 min.

Because the experiments had been conducted over a short period of time relative to that for processes in the lake, studies were conducted to assess changes which took place over a 24 hr reaction period. A series of samples of offshore water were equilibrated with cadmium for 24 hr, to determine both the complex forming capacity and the stability constant. The complex forming capacity was 3.5×10^{-8} M compared to 2.8×10^{-8} M for the shorter equilibration time, and the conditional formation constant was increased from 12×10^{7} to 16×10^{7}. Results of one experiment are shown in Figure 1. For the sample which had been membrane filtered, the initial rapid ASV signal decrease shown in Figure 1a was equivalent to that which had been measured in the short-term uptake experiments. The rapid decrease was followed by a slower decrease in signal beginning 4 hr after the addition of the cadmium. The rate constant for the reaction was $0.009\ h^{-1}$ and the reaction was not

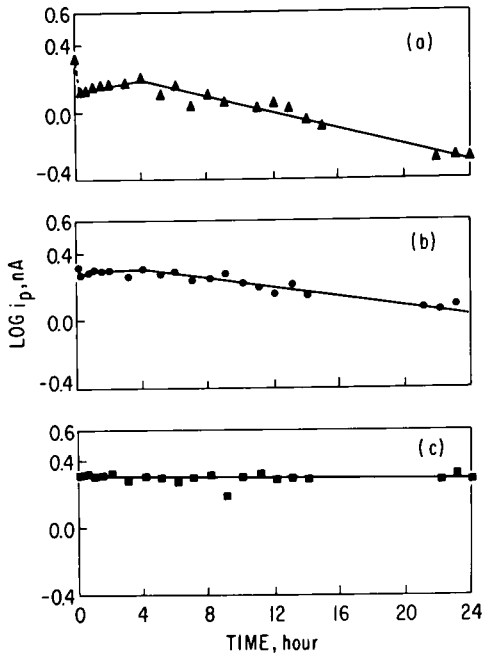

FIG. 1.--Plots of the logarithm of the ASV signal (log i_p) versus time after the addition of a cadmium spike. Sample treatments: (a) membrane filtration, (b) ultrafiltration, and (c) uv irradiation of membrane filtered samples. (ANL Neg. 149-89-259)

complete within the 24 hr period studied. As shown in Figure 1b, cadmium added to the ultrafiltrate reacted in the same way as the 0.45 μm filtrate except for the lack of an initial rapid uptake period. The rate constant in the ultrafiltrate was 0.007 h^{-1} which is similar to the 0.009 h^{-1} value for the 0.45 μm filtrate. No reaction of cadmium occurred in the sample which had been uv irradiated (Figure 1c), indicating that both the cadmium complexing material which is retained by an ultrafilter and that which passes through the ultrafilter are organic compounds.

The results indicate that cadmium can be taken up by colloids within a short period. Cadmium undergoes a slower reaction with soluble matter. The results of uv irradiation indicate that both the colloidal and soluble matter in Lake Michigan which react with cadmium are organic.

These results suggest that little of the cadmium in Lake Michigan is in a free ionic state. For an added 0.5 μg Cd/L, which would approximately double the present concentration of cadmium, it is estimated that only 14% would remain free after 24 hr. It should be noted that equilibrium has not been attained within 24 hr. In the lake the fraction of the cadmium in the free ionic state would be expected to be significantly less since the lake would be closer to true

chemical equilibrium because of its long residence time and the slower rate of cadmium addition to the lake.

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COLLOIDAL MATERIAL IN LAKE MICHIGAN*

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A study of the reaction of cadmium with components of Lake Michigan water[1] has indicated that about two-thirds of a 1 μg Cd^{2+}/L addition reacts with the colloidal material present. This suggests that the colloids be studied with regard to their physical and chemical properties. Numerous previous studies have been concerned with particulate material larger than 0.45 μm. Although the majority of the particulate mass for lake water samples is contained in the larger material, the colloids which pass through the filter should be expected to have both greater numbers and surface area.

Lake Michigan water samples were collected both at the shore in Chicago and approximately 20 miles offshore and were filtered through a 0.45 μm membrane filter. This filtrate was then filtered through a Biofiber 80 miniplant ultrafilter containing cellulose acetate hollow fibers with a molecular weight cutoff of approximately 30,000, which operationally separated soluble and colloidal matter. The colloids were removed by backflushing with ultrafiltrate to provide a 50-fold concentration of the colloids.

Aliquots of these samples were placed in an ultrasonic cleaner for one-half hour to disperse the colloidal particles. A sample was then placed on an electron microscope grid which had been covered with a thin Formvar sheet. The grid was covered and air-dried at room temperature prior to transmission electron microscopic examination. From photographs of 10,000- to 50,000-fold magnification, the number and size of the colloids have been measured.

Number, mean diameter, surface area, and weight of the colloids are presented in Table 1. Since the characteristics will be by drying, the reported size is a minimum for these samples. The number of particles present in various

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Table 1. Characteristic of colloids of Lake Michigan water.

Month (1977)	Location	No/L	Mean diameter, μm	Surface area, cm^2/L	Weight,[a] μg/L
June	offshore[b]	6.66×10^{12}	0.035	376	418
September	offshore[b]	1.21×10^{13}	0.032	466	323
June	at shore[c]	4.51×10^{12}	0.055	575	894
October	at shore[c]	2.70×10^{12}	0.086	680	1,100
November	at shore[c]	3.50×10^{12}	0.068	546	706

[a]Unit density assumed.

[b]Latitude 43°00'22"; longitude 86°22'12".

[c]31st Street pier, Chicago, Illinois.

size groups is shown in Figure 1. The characteristics of the colloids collected at shore are similar for the three samples collected between June and November. The average number of colloids present was 3.6×10^{12}/L, and the average diameter and surface area were approximately 0.07 μm and 600 cm^2/L, respectively. If the density of the colloids is assumed to be 1 g/cm^3, then the average weight of colloids is 0.9 mg/L. The number of colloids in the offshore samples was 9.4×10^{12}/L, which was 2-1/2 times greater than the number in the samples collected at shore. However, because the average diameter of the samples collected offshore was only 0.03 μm, the average surface area was calculated to be 400 cm^2/L and the weight of colloidal material was estimated to be less than 400 μg/L. For reaction with added metal ions, the parameter of greatest importance is the surface area. There was little difference in the surface areas of the colloids in the three samples collected at shore, and their areas were only 50% greater than the surface areas of the colloids in the offshore samples.

Analysis of total organic carbon in the samples, together with the estimated weight of colloids, indicates that these colloids contain 30 to 40%

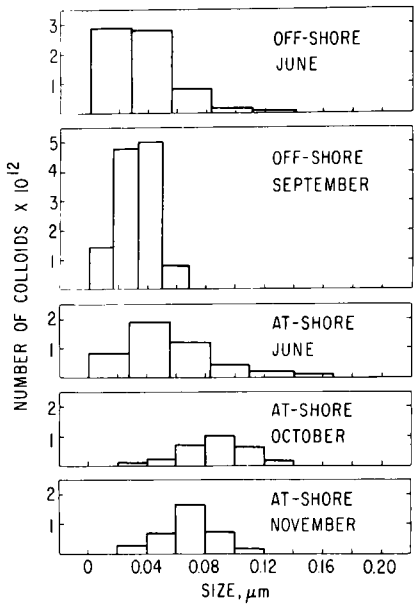

FIG. 1.--Distribution of sizes of colloidal particles in samples.
(ANL Neg. 149-78-260)

carbon, suggesting that organic compounds constitute a major portion of the colloidal material. Following ultraviolet irradiation of the sample plus hydrogen peroxide, no colloids were observed in the electron micrographs. Total organic carbon analyses of these samples were indistinguishable from those for blanks.

Although the nature of the colloidal matter has not yet been elucidated, the colloids are predominantly organic and are of significance with regard to their reactions with trace metals.

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DISTRIBUTION PROFILES OF INDUSTRIALLY-DERIVED ^{238}Pu AND FALLOUT $^{239,240}Pu$ IN SOILS OF THE GREAT MIAMI RIVER WATERSHED, OHIO

C. M. Bobula and J. J. Alberts*

Plutonium disseminated to the terrestrial environment as a result of both weapons testing and releases from nuclear processing facilities is ecologically significant as a contaminant which is potentially available for biological uptake. The preponderance of published literature relevant to the behavior of plutonium in soils pertains to investigations conducted in arid or semi-arid climates.[1] Postdepositional resuspension of respirable soil particles enhances the availability of plutonium to desert rodents and plant surfaces.[2] However, in prairie and forested soils of temperate regions, particulates are less subject to airborne redistribution, owing largely to well-established vegetational cover and moderately high annual precipitation (91 cm). Distributions of long-lived radionuclides ($^{239,240}Pu$ and ^{137}Cs) from weapons fallout and industrially-derived ^{238}Pu were determined in Midwestern soils sampled near Mound Laboratory in Miamisburg, Ohio.

The study site represents an urban-agricultural environment impacted by plutonium deposition from both fallout and Mound Laboratory, where weapons components and radioisotopic heat sources are manufactured. Therefore, the mobility of plutonium from two different sources may be compared in various soils of this watershed. The study area and activity values for ^{238}Pu and $^{239,240}Pu$ in surface soils have been described previously.[3,4]

Soils for analysis were collected in two pastures and two woodlots outside the influence of atmospheric releases of Mound Laboratory in Hueston Woods, located 65 km west of Miamisburg and in Urbana, 80 km northeast of Miamisburg. Soils within the range of Mound Laboratory emissions were sampled in Mound State Park (400 m east of Mound Laboratory stacks) and Library Park (1 km north). Depth increments of 2.5 cm were successively removed from a

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10 cm × 20 cm section of soil at all locations, oven-dried (105°C) and ground to pass a 1 mm screen prior to analysis for plutonium and cesium.[5]

Concentrations of ^{238}Pu, $^{239,240}Pu$, and ^{137}Cs per unit weight are reported in Tables 1 and 2. Vertical distributions reflect nuclide concentration values per unit area (Figures 1 and 2).

Depth profiles of ^{238}Pu, $^{239,240}Pu$, and ^{137}Cs are similar in each background soil sampled (Figure 1). Both ^{238}Pu and $^{239,240}Pu$ were introduced to these areas as fallout, with the major input occurring between 1957 and 1963. A significant quantity of ^{238}Pu was also introduced as a result of the SNAP-9A burnup in 1964. The similarity of ^{137}Cs and plutonium profiles is not surprising if the mechanism of mobilization for both is via the movement of particles with attached nuclides, since leading from soil and movement in solution would be expected to result in obviously different depth profiles, due to the differences in chemical behavior of the two elements.[6] Activity measurements in sediment cores from Lake Michigan have also produced a strong correlation between plutonium and ^{137}Cs distributions to profile depths of 8 cm.[7] Individual profile characteristics apparently reflect the site-specific effects of bioperturbation and edaphic factors such as structure, organic matter content, and permeability on the mechanical movement of fine soil particles. Pastures sampled at Hueston Woods (HWP) and Urbana (UOP) exhibit virtually identical nuclide distributions, attributable perhaps to comparable soil permeabilities. In both locations, natural soil structure in the uppermost layers has been similarly altered due to compaction by grazing animals. Disparities in the plutonium profiles of Hueston Woods woodlot (HWW) and Urbana woodlot (UOF) lend further support to the concept of movement by particles. Incremental bulk densities, particularly in the surface layer of UOF (0.55 g/cc) are consistently lower than those of HWW, where bulk density in the upper 2.5 cm is 1.07 g/cc. Admittedly, particle movement may vary as a function of many other soil characteristics. In these two soils, however, distribution ratios very closely parallel relative differences in bulk density.

Concentration values for ^{238}Pu in Mound State Park (MSP) and Library Park (LP) are noticeably elevated as a result of Mound Laboratory emissions.

Table 1. Fallout ^{238}Pu, $^{239,240}Pu$ and ^{137}Cs (pCi/kg dry wt)[a] in Miami River watershed soils.

Depth of sample (cm)	Hueston Woods woodlot	Hueston Woods pasture	Urbana-Oberly woodlot	Urbana-Oberly pasture
	^{238}Pu $^{239,240}Pu$ ^{137}Cs	^{238}Pu $^{239,240}Pu$ ^{137}Cs	^{238}Pu $^{239,240}Pu$ ^{137}Cs	^{238}Pu $^{239,240}Pu$ ^{137}Cs
0—2.5	0.97 ± 0.11 24.0 ± 0.5 1500 ± 30	0.73 ± 0.07 17.5 ± 0.3 984 ± 24	1.32 ± 0.11 21.8 ± 0.4 1270 ± 10	1.13 ± 0.09 26.3 ± 0.4 1440 ± 20
2.5—5.0	0.55 ± 0.08 12.2 ± 0.3 567 ± 18	0.56 ± 0.06 14.6 ± 0.3 774 ± 19	1.36 ± 0.10 27.9 ± 0.4 1520 ± 10	0.85 ± 0.10 22.6 ± 0.4 1140 ± 20
5.0—7.5	0.23 ± 0.04 5.28 ± 0.14 239 ± 9	0.39 ± 0.04 9.36 ± 0.18 460 ± 6	0.80 ± 0.07 20.4 ± 0.3 1080 ± 20	0.40 ± 0.06 11.7 ± 0.2 553 ± 10
7.5—10.0	0.14 ± 0.05 3.48 ± 0.15 140 ± 6	0.15 ± 0.05 4.68 ± 0.14 240 ± 5	0.42 ± 0.05 12.2 ± 0.1 527 ± 9	0.06 ± 0.02 4.34 ± 0.09 210 ± 6
10.0—12.5	0.06 ± 0.03 2.32 ± 0.08 117 ± 6	0.16 ± 0.03 3.32 ± 0.09 164 ± 5	0.15 ± 0.03 4.60 ± 0.17 187 ± 7	0.03 ± 0.03 1.49 ± 0.06 115 ± 5
12.5—15.0	0.13 ± 0.04 1.88 ± 0.09 81.1 ± 5.6	0.09 ± 0.03 2.44 ± 0.09 138 ± 5	0.09 ± 0.03 2.80 ± 0.09 112 ± 6	0.06 ± 0.02 2.24 ± 0.06 83.9 ± 5.1

[a] The ± value is 1 σ counting error.

Table 2. ^{238}Pu, $^{239,240}Pu$ and ^{137}Cs (pCi/kg dry wt)[a] in soils proximate to Mound Laboratory.

Depth of sample, cm	Mound State Park	Library Park
	^{238}Pu	^{238}Pu
	$^{239,240}Pu$	$^{239,240}Pu$
	^{137}Cs	^{137}Cs
0—2.5	3320 ± 50	147 ± 3
	33.0 ± 4.8	41.3 ± 1.5
	1230 ± 30	2190 ± 50
2.5—5.0	2480 ± 30	75.5 ± 2.2
	27.8 ± 3.6	33.6 ± 1.5
	1150 ± 20	1540 ± 30
5.0—7.5	1980 ± 20	13.3 ± 1.1
	21.9 ± 3.3	9.16 ± 0.09
	800 ± 21	447 ± 9
7.5—10.0	743 ± 16	4.48 ± 0.30
	11.0 ± 1.9	3.71 ± 0.27
	426 ± 16	169 ± 6
10.0—12.5	435 ± 5	3.06 ± 0.22
	7.71 ± 0.06	1.83 ± 0.17
	212 ± 6	133 ± 21
12.5—15.0	131 ± 2	1.01 ± 0.10
	2.58 ± 0.35	1.10 ± 0.10
	118 ± 6	51.1 ± 6.5
15.0—17.5	65.6 ± 1.7	0.87 ± 0.09
	2.89 ± 0.37	1.10 ± 0.09
	71.4 ± 5.3	36.5 ± 8.8
17.5—20.0	39.2 ± 1.4	0.21 ± 0.03
	0.80 ± 0.02	0.66 ± 0.04
	31.0 ± 7.0	33.5 ± 7.4

[a]The ± value is 1 σ counting error.

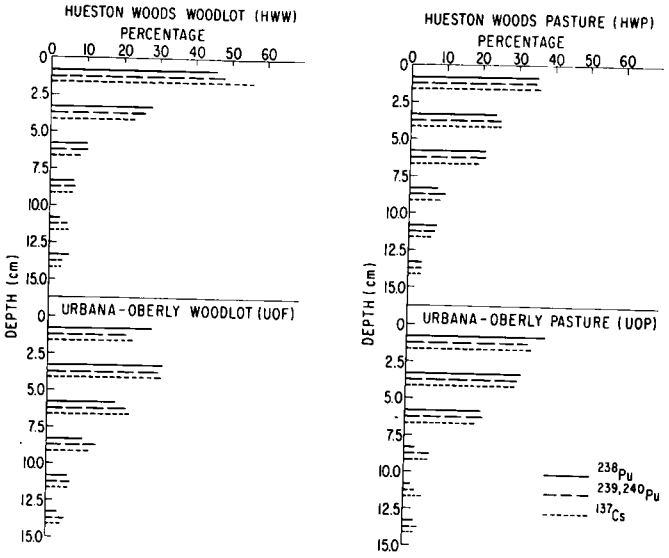

FIG. 1.--Vertical profiles of fallout ^{238}Pu, $^{239,240}Pu$, and ^{137}Cs in four Miami River Watershed soils. (The fraction in each layer is represented as a percentage of the total nuclide activity found in the upper 15 cm of soil.) (ANL Neg. 149-78-263)

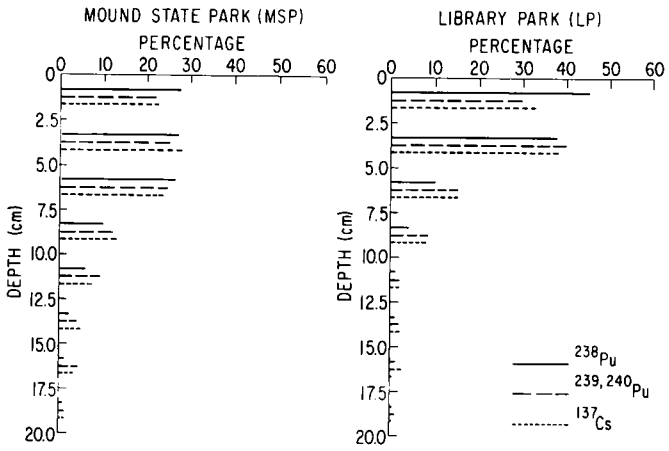

FIG. 2.--Vertical profiles of ^{238}Pu, $^{239,240}Pu$, and ^{137}Cs in soils proximate to Mound Laboratory. (The fraction in each layer is represented as a percentage of the total nuclide activity found in the upper 20 cm of soil.) (ANL Neg. 149-78-262)

^{238}Pu in these soils has been deposited recently, as indicated by a comparison of relative ^{238}Pu, $^{239,240}Pu$, and ^{137}Cs distributions in the top 2.5 cm of soil.

Although biological perturbation of our soil profiles cannot be demonstrated at this time, investigations of the effects of soil fauna on soil translocation seem necessary in assessing the importance of organismal activity. The burrowing and feeding activities of natural populations of tubificid oligochaetes are known to blur sediment stratigraphy in Lake Michigan to a depth of 10 cm.[8] It is probable that earthworms, diplopods, and isopods also influence radioactivity profiles in terrestrial systems. Earthworms (Allalobophora) live

and, to a large extent, feed within the soil layers of woodlands and pastures, consuming large quantities of mineral matter when feeding. In arable orchard soils, Lumbricus terrestris populations have been observed to consume over 93% of the annual leaf-fall (2000 kg of leaf litter per ha).[9]

The source of aerially deposited ^{238}Pu in the environs of Mound Laboratory has little, if any, effect on postdepositional mobility. Features of a particular soil profile seem to be governed by biological and edaphic factors influencing the movement of particles with which plutonium and cesium are associated, rather than by solution chemistry.

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PLUTONIUM IN THE GREAT MIAMI RIVER, OHIO—SUMMARY OF AN EXPERIMENT CONDUCTED IN OCTOBER 1976

D. N. Edgington, C. W. Kennedy, G. E. Bartelt, and C. M. Bobula

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The behavior of the plutonium isotope, ^{238}Pu, is being studied in the Great Miami River watershed. One of the objectives is to establish the fate and elucidate any changes in chemical form of dissolved plutonium that is discharged from time to time from the Mound Laboratory in the form of low-level liquid waste. In this type of experiment a dye (Rhodamine WT) is added to the tank prior to discharge and the contents are thoroughly mixed. Observation of the dye provides the means for establishing the location of the plutonium-bearing pulse, and hence, the time at which the samples should be taken at the stations downstream. In a previous report,[1] we discussed the results of two earlier experiments of this type.

Another experiment was carried out in October 1976. It was similar to those carried out previously but had been significantly expanded with respect to both the number of sampling sites downstream and the number of samples taken at each site. Unexpectedly, the amount of plutonium in the release was almost two orders of magnitude lower than that encountered in previous releases, ~ 0.5 μCi rather than 18 and 24 μCi. As a result, the only location in the river at which the concentration of ^{238}Pu was found to be significantly higher than the background concentration was at the first sampling point, Chautauqua, which is 2.4 km below the discharge point.

Although the original objectives of the experiment could not be realized because of the extremely low amount of ^{238}Pu released, the data obtained have provided valuable information contributing to our understanding of the contribution of various sources to the total plutonium transported by the river. The latest results confirm earlier observations that the amount of plutonium being transported by the water and suspended particles is much larger than can be accounted for by the periodic effluent releases alone.[2]

Documented releases of ^{238}Pu to the Great Miami River varied between 16 and 20 mCi for the period 1973–1975.[3–5] In 1976 when changes were made

in the waste management procedures, the total discharge was only 3 mCi.[6] Despite the ~100-fold decrease in the amount of plutonium being released in the effluent pulses, the plutonium in the river, almost entirely on the suspended particles, has remained quite constant. In October 1976 the concentration at Franklin (9.7 km below the discharge point) before, during, and after the pulse was 12 fCi L^{-1}. This is essentially the same concentration as that found prior and subsequent to the passage of pulses in 1975, 14 fCi L^{-1}. As the mean annual flow rate for the river at Franklin is ~2200 cfs,[7] this concentration corresponds to a daily flux of about 60 μCi and an annual flux of about 23 mCi. This annual flux is almost an order of magnitude greater than that due to the known releases in 1976.

There are two possible sources for this additional supply of plutonium to the river. They are either a reservoir of plutonium-bearing sediments in the river itself resulting from previous releases, or a continuous leakage of plutonium deposited in the North or South canals (which are known to be contaminated with ~5 Ci of ^{238}Pu)[8] between the Mound Laboratory and the river. Since there is no longer a direct connection between the North Canal and the river, the most likely source is the 3.2 Ci of ^{238}Pu in the South Canal[8] which drains into the river via Overflow Creek.

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URANIUM IN WATER AND SUSPENDED SEDIMENTS OF THE GREAT MIAMI RIVER, OHIO

C. W. Kennedy, G. E. Bartelt, and K. A. Orlandini

The concentrations of ^{238}U and ^{234}U were measured in water and suspended sediment samples collected during a dye tracer experiment in the Great Miami River during October 1976. (The dye was used to follow the release and dispersion of Mound Laboratory effluent containing low levels of ^{238}Pu.) Results from uranium analyses of samples taken downstream of the discharge point show no relationship to the movement of ^{238}Pu, nor to distance from the release site (Table 1). It appears that uranium concentrations in the river are unaffected by the effluent from Mound Laboratory. This conclusion will be verified by analyzing pipe effluent and upstream water for uranium.

Each sample reported here consisted of one gallon of water filtered through a 0.45 μm Millipore membrane. Sample locations were Franklin (6 river miles downstream of the discharge pipe) and Trenton (16 river miles downstream from the pipe). Collections occurred at various times during the passage of the effluent through the sampling site.

The average concentration of ^{238}U in Great Miami River water is 0.59 pCi/L (Table 1). This is approximately 6 times the average ^{238}U concentration (0.1 pCi/L) for Lake Michigan water (Orlandini and Wahlgren, unpublished data). The difference is probably due to variation in availability of uranium between the two drainage basins. The $^{234}U/^{238}U$ ratios in water from both regions are similar, 1.2 for Lake Michigan[1] and 1.15 for the Great Miami River.

The average uranium distribution coefficients (K_d's) between suspended particles and the dissolved phase for the Great Miami River are 1.8×10^3 for ^{238}U and 1.6×10^3 for ^{234}U. These values are comparable to the ^{238}U K_d reported for Lake Michigan of 1×10^3.[2] The K_d's calculated for ^{238}Pu and $^{239,240}Pu$ in both the lake and the river are about 10^5.[2] This indicates that plutonium has greater affinity for particles than uranium by two orders of magnitude.

Table 1. Uranium concentrations in the Great Miami River during an effluent pulse.

Site/time	Filtered water, pCi/L			Suspended sediment, pCi/g			K_d[a]	
	^{238}U	^{234}U	$^{234}/^{238}U$	^{238}U	^{234}U	$^{234}/^{238}U$	^{238}U	^{234}U
Franklin								
Before	0.66[b]	0.76	1.14	2.88	0.91	0.91	4.4×10^3	3.4×10^3
Peak	0.66	0.77	1.17	0.77	0.99	1.28	1.2×10^3	1.3×10^3
Down	0.56	0.61	1.09	1.01	1.07	1.06	1.8×10^3	1.8×10^3
Down	0.52	0.57	1.10	0.99	1.11	1.12	1.9×10^3	1.9×10^3
Down	0.59	0.66	1.12	0.51	0.56	1.10	0.86×10^3	0.86×10^3
Down	0.54	0.61	1.13	1.03	1.08	1.04	1.9×10^3	1.8×10^3
Trenton								
Before	0.72	0.86	1.19	1.05	1.00	0.95	1.5×10^3	1.2×10^3
Before	0.56	0.70	1.25	0.83	0.90	1.08	1.5×10^3	1.3×10^3
Peak	0.56	0.61	1.09	0.85	0.80	0.94	1.5×10^3	1.3×10^3
Down	0.59	0.69	1.17	0.83	1.01	1.22	1.4×10^3	1.5×10^3
Down	0.57	0.66	1.16	0.80	0.85	1.06	1.4×10^3	1.3×10^3
Averages	0.59	0.68	1.15	1.05	1.09	1.04	1.8×10^3	1.6×10^3

[a] Not an actual K_d measure of uranium affinity for suspended particles since much of the uranium present in the mineral phases is normally unavailable to the water. In the analytical procedure, mineral structure is broken down during acid leaching.

[b] The counting error for each sample is <5%.

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SEASONAL CYCLING OF PLUTONIUM IN THE WATER COLUMN OF LAKE MICHIGAN: 1975–1977

M. A. Wahlgren, D. M. Nelson, and E. T. Kucera

Data from a 4-year period were recently summarized[1] to show that the total (particulate and dissolved) plutonium concentration in the surface waters of Lake Michigan vary annually in a well-defined pattern. Loss of dissolved plutonium from the epilimnion requires its adsorption and transport on settling particulate matter; the constancy of the distribution of plutonium between dissolved and particulate phases has been demonstrated for Lake Michigan.[2] It is known that most of the diatoms settling in Lake Michigan dissolve in the water column.[3] Microscopic observations of calcite patricles from filters and sediment traps indicate similar fates for these authigenic particles. It is, therefore, of interest to study the depth distribution of both the dissolved and particulate forms of plutonium.

In Figure 1a, the isopleths of dissolved plutonium are shown over the 3-year period for which data are available (the presence of a thermocline is indicated by the shaded regions in the figure). From these isopleths, the concurrent measurements of particulate-bound plutonium (which rarely exceeds 20% of the total), it is clear that the seasonal cycle involves removal of a significant fraction of the plutonium from the water column down to depths as great at 60 m. During fall turnover (late November) each year, the concentration of dissolved plutonium becomes uniform in the water column from the surface to 60 m, at a value near 0.35 fCi L^{-1}. In contrast, the concentrations of particulate matter (and its associated plutonium) present during the December sampling at station 5 are highly variable from year to year. During the relatively mild winters prevailing in the decade prior to the winter of 1976–77, wind-driven vertical mixing could occur from fall turnover to the onset of summer stratification; mixing during this several-month period would provide an opportunity for replenishment of dissolved plutonium concentrations from resuspended benthic particulates.

Although the inputs of new fallout since the plutonium study began (1972) are nearly trivial compared to the cumulative deposition onto the lake, those

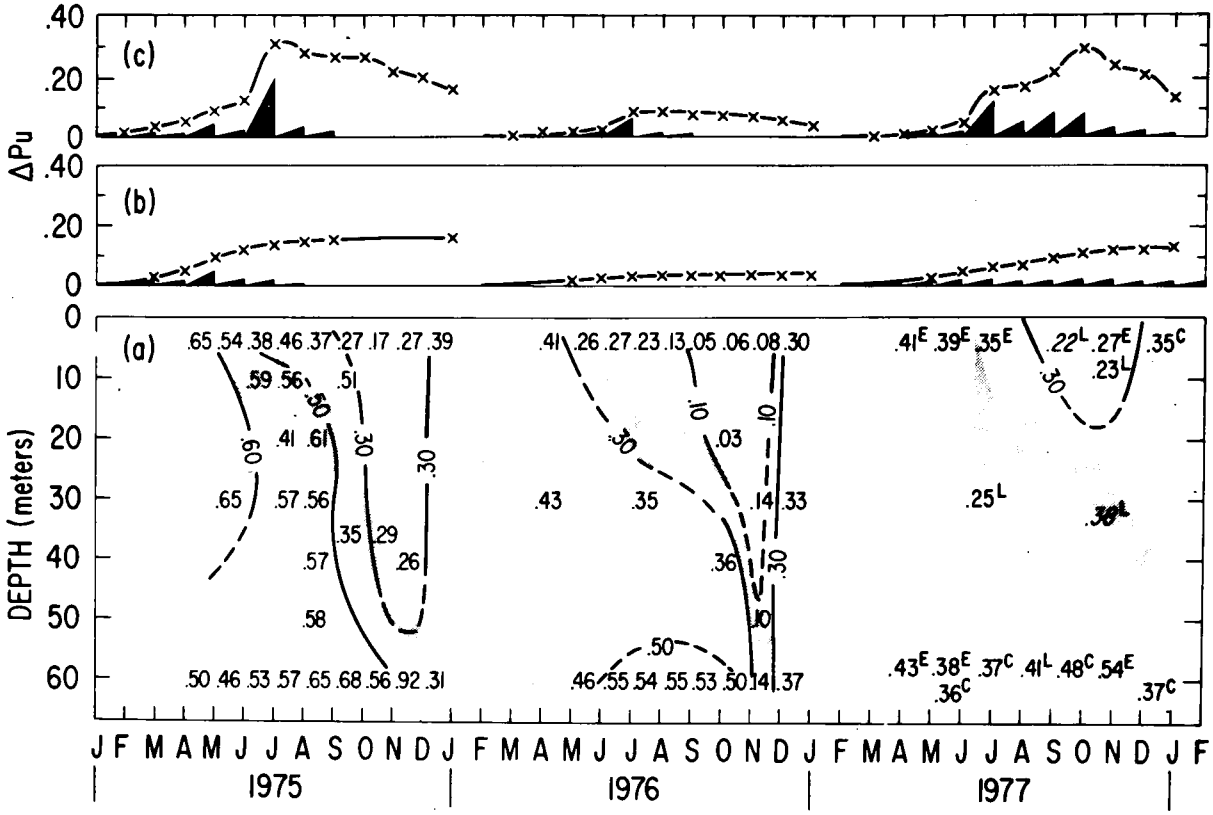

FIG. 1.--Seasonal cycling of dissolved plutonium in Lake Michigan during a period of variable fallout inputs. The development and breakdown of thermoclines are indicated by shaded regions on the graph. (ANL Neg. 149-78-226)

during 1974, 1975 and 1977 are not insignificant compared to the present loading of the water column. In Figure 1b, the increase in plutonium concentration expected in a well-mixed lake of 84 m mean depth is plotted on a monthly basis (solid area), and integrated over the year (solid curve). The maximum increases which could occur if the new input were totally retained in the eplimnion are shown in Figure 1c. The low plutonium concentrations observed through the water column in late summer of 1976 apparently result from a combination of factors, i.e., an unusually warm and sunny spring season, little input of new fallout into the Great Lakes, and efficient scavenging by calcite particles. The distribution of plutonium between dissolved and particulate was found to be the same during 1975 and 1976; this observation, together with the similar concentrations of dissolved plutonium present following fall turnover each year, are consistent with earlier conjectures that the new

inputs are rapidly assimilated into a much larger plutonium pool which must include the surficial sediments, and perhaps the entire mixing layer described by Robbins and Edgington.[4]

The initial removal of plutonium from surface waters is coincident each year with the spring diatom bloom and apparently is restricted to the upper euphotic zone. Precipitation and settling of calcite have been observed qualitatively during August and September for each year of the study, coincident with the second phase of plutonium removal. Dissolved silica concentrations in the 60 m of the water column have been shown to be low from June until September[5] when the concentration rises rapidly in the hypolimnion. Little if any increase in plutonium in the hypolimnion occurs in late summer; apparently plutonium which is released on dissolution of frustules is sorbed by resuspended surficial sediment flocs.

The data shown are primarily from a single sampling station, ANL-5 (12 km SW of Grand Haven, Michigan), but the same trends have been observed at stations further offshore, including ANL-18 in the middle of the southern basin. Further offshore, the onset of stratification occurs later in the spring season, and the initial removal of plutonium from surface waters is delayed correspondingly. At these stations, the concentrations of plutonium in the hypolimnion show relatively little decrease from 1975 to 1977. This observation is not unexpected in view of the much larger hypolimnetic volume present in mid-lake and the low sedimentation rate.

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A COMPARISON OF THE CONCENTRATIONS OF FALLOUT-DERIVED PLUTONIUM IN A SERIES OF FRESHWATER LAKES

M. A. Wahlgren, J. J. Alberts,* K. A. Orlandini, and E. T. Kucera

The concentrations of fallout-derived plutonium and its distribution among physicochemically-defined fractions in several natural water systems including Lake Michigan have recently been reported.[1] During 1977, comparison samples were obtained from a series of Canadian lakes having a wider range of limnological parameters, in collaboration with the Freshwater Institute of Environment Canada. To obtain samples representative of mean lake conditions, samples were taken during the mixing periods preceding summer stratification or following fall turnover.

Comparison data from previous studies on the Great Lakes, from the cited study of physicochemical forms of plutonium, and from the series of Canadian lakes are presented in Table 1. The radionuclide concentrations are given in moles L^{-1} to facilitate comparison to thermodynamic data on the solubilities of various plutonium species.[2] Comparison of plutonium concentrations to those of naturally-occurring ^{232}Th (the geochemical analog of Pu IV) indicates a stronger covariance of these two radioelements in these natural systems than might have been expected in view of the different source terms and equilibation times within the systems.

In Figure 1 the concentrations of plutonium and thorium are expressed as a function of pH. Within the alkaline range, the concentrations of dissolved plutonium in the comparison lakes are generally similar to those found within the Great Lakes. A considerably higher concentration of plutonium is found in lake 13 (a highly saline lake) and in lake 10 (a eutrophic-alkaline lake). The concentrations of plutonium in natural waters with pH < 7 are higher on the average by about a factor of ten. Significantly greater concent rations of plutonium are found at and below the chemocline in lake 12 (an iron-meromicitic

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Table 1. Comparison of plutonium concentrations and chemical variables[a] in freshwater lakes.

Key	Lake	Year sampled	pH	Alkalinity (as $CaCO_3$), mg L^{-1}	Conductivity, mhos cm^{-1}	Cl^-, mg L^{-1}	$SO_4^=$, mg L^{-1}	Pu, $ML^{-1} \times 10^{-17}$	Th, $ML^{-1} \times 10^{-11}$
Great Lakes									
1	Michigan	1977[b]	8.2	113	220	6	16	2.1	3.0
2	Huron	1973—76	8.0	79	200	6	17	2.3	
3	Erie	1973—76	8.1	92	310	25	26	0.5	
4	Ontario	1973—76	7.9	93	270	28	29	1.0	
5	Superior	1973	7.8	52	95	1	4	2.2	
Canadian Lakes									
6	Clear (Manitoba)	1977	8.0	190	300			4.6	22
7	Last Mountain (Saskatchewan)	1977	8.4	305	3000	180	1300	4.5	6.8
8	Katherine (Manitoba)	1977	8.5	180	240			2.8	7.6
9	Lake of the Woods (Ontario)	1977	7.1	50	95	3	6	2.4	8.3
10	AELA 885 (Manitoba)	1977	8.4	355	1200	35	500	7.4	44
11	ELA 661 (Ontario)	1977	4.8		25	~1	low	44	65
12a	ELA 241 surface	1977	5.9	<10	32		low	29	60
12b	ELA 241 9 m	1977	6.0	~30	~70			48	110
12c	ELA 241 11 m	1977	6.1	--	~350			≥220	--
13	Little Manito (Saskatchewan)	1977	8.0	770	>2000		$\sim 10^5$	47	≥30
14	Great Slave Lake (main basin)	1977	8.2	80	155	~1		1.5	
15	Great Slave Lake (Christie Bay)	1977	8.5	65	135	8.5	30	2.9	
16	Great Slave Lake (McLeod Bay)	1977	7.5	15	30	0.5	low	3.7	
SE United States									
17a	Banks (Georgia)	5/1975	3.9		--			20	
17b	Banks (Georgia)	12/1975	4.0		--			5	
18	Okeefenokee (Florida)		5.0		--			15.4	
19	Par Pond (Georgia)	2/1976	3.0	~15	~50	5	4	0.5	
	World average freshwater		--	~50	--	8	11		

[a] The limnological data used to construct this table were derived in part from the summaries compiled by the Great Lakes Basin Commission,[4] Armstrong and Schindler,[5] and Clarke.[6]

[b] Pu values given for Lake Michigan are mean concentrations observed in hypolimnetic samples during 1977.

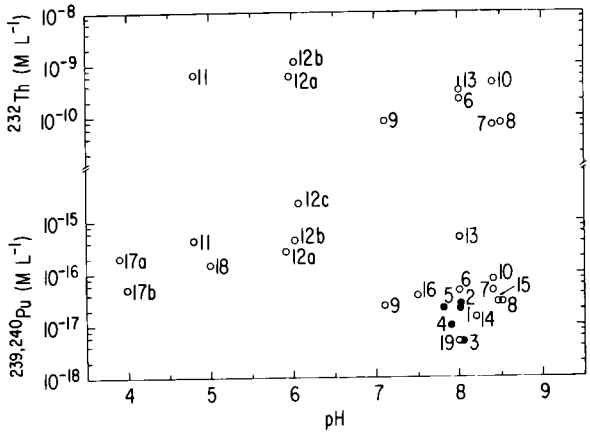

FIG. 1.--pH dependence of the concentrations of plutonium and thorium in freshwater lakes (● Great Lakes, O comparison lakes).
(ANL Neg. 149-78-230)

lake), where highly reducing conditions are known to prevail, than in the surface waters.

Preliminary data from the current investigation confirm the previous finding[1] that a large proportion of the dissolved plutonium in lakes with pH < 7 is present in nonionic forms. In the following article[3] it will be shown that the occurrence of high concentrations of dissolved plutonium is coincident with a higher proportion of Pu IV, as would be expected from the observed covariance of concentrations of plutonium and thorium.

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STUDY OF THE OCCURRENCE OF MULTIPLE OXIDATION STATES OF PLUTONIUM IN NATURAL WATER SYSTEMS

M. A. Wahlgren, J. J. Alberts,* D. M. Nelson, K. A. Orlandini and E. T. Kucera

Plutonium is the only chemical element for which four oxidation states can coexist in an aqueous solution. Therefore, the determination of the relative abundances of various oxidation states of plutonium present in natural waters is necessary to the understanding (in both field and laboratory studies) of measured distributions of plutonium between dissolved and solid phases. ^{237}Pu VI (in the presence of residual perchlorate ion from the oxidation procedure) has been found to remain in that oxidation state for at least 1 month when added to filtered Lake Michigan water. Thus, earlier assumptions that Pu IV is the more stable form of plutonium in natural waters may be in error, at least for the important class of oligotrophic, high-carbonate lakes. In order to test this hypothesis, we investigated the oxidation states of plutonium present in Lake Michigan water samples throughout the field season, and in comparison samples from Canadian lakes having a wider range of chemical and other limnological properties.[1]

Three independent analytical procedures which can fractionate the higher (V, VI) from the lower (III, IV) oxidation states of plutonium have been applied to Lake Michigan samples. The results show that ≥80% of the dissolved plutonium (< 0.45 μm) is present as Pu V or VI, while ≤ 10% of the plutonium found adsorbed on natural particulate matter is in these oxidation states. Also, naturally-occurring uranium (VI) neither exhibits significant sorption on particulate material nor undergoes seasonal cycling in the water column. These results strongly suggest that reduction of plutonium from VI (or V) to IV is a major factor in controlling its distribution between dissolved and particulate phases.

Additions of various plutonium isotopes in known oxidation states (IV or VI) to natural and amended Lake Michigan water samples showed that (1)

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oxidation-reduction reactions can occur during times much shorter than the annual cycling of plutonium in the lake, and (2) the rates of redox reactions of fallout-derived plutonium present in the lake water are significantly different from those of either the Pu IV or Pu VI spikes. Therefore, new inputs of soluble plutonium from the same or different sources can be expected to attain a steady-state distribution of oxidation states (probably a mixture of IV, V, and VI) in the water column within a few months. This conclusion is consistent with previous observations[2] that (1) the distribution of plutonium between dissolved forms and suspended particulate phases is essentially invariant in Lake Michigan surface waters, even when newly-deposited fallout plutonium must contribute a significant fraction of the total, and (2) the distributions in other alkaline aqueous systems for plutonium derived from various source terms are relatively similar to that in Lake Michigan.

The results from the comparative lake study are shown in Table 1. The concentrations of dissolved plutonium in higher oxidation states are found to be quite similar in all of the alkaline lakes, while those of the lower oxidation states are much more variable. These data suggest that Pu IV is more efficiently scavenged from solution in the oligotrophic alkaline lakes. The ratio of higher to lower oxidation states of dissolved plutonium appears to be independent of pH (Figure 1), and can be related qualitatively to chemical characteristics of the lakes.[1] The concentrations of plutonium in the higher oxidation states are well correlated with measured alkalinities, while those of the lower oxidation states are much more variable.

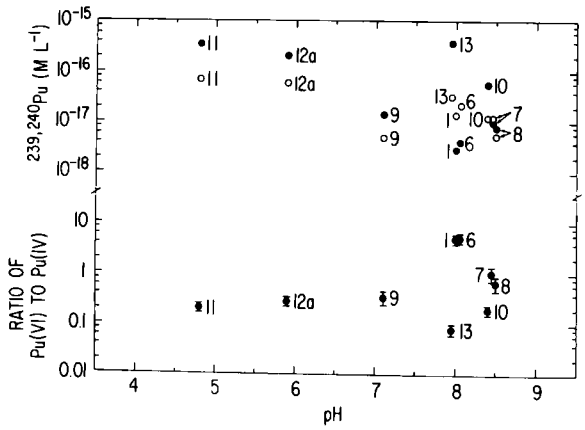

FIG. 1.--Distribution of concentrations and ratios of plutonium oxidation states in freshwater lakes (O concentration of Pu VI, ● concentration of Pu IV, ⧓ ratio of concentrations). For explanation of numbers, see Table 1. (ANL Neg. 149-78-229)

Table 1. Comparison of concentrations of Pu in the IV and VI oxidation states in freshwater lakes.

Key No.	Lake	Concentrations				Ratio of Pu VI to Pu IV
		Pu IV		Pu VI		
		fCi L^{-1}	ML^{-1}	fCi L^{-1}	ML^{-1}	
1	Michigan	0.06 ± 0.02	0.3	0.32 ± 0.08	1.5	5.3 ± 1.8
6	Clear (Manitoba)	0.09 ± 0.02	0.4	0.47 ± 0.04	2.2	5.2 ± 1.0
7	Last Mountain (Saskatchewan)	0.25 ± 0.06	1.2	0.25 ± 0.03	1.2	1.0 ± 0.3
8	Katherine (Manitoba)	0.18 ± 0.08	0.8	0.12 ± 0.04	0.55	0.67 ± 0.20
9	Lake of the Woods (Ontario)	0.32 ± 0.08	1.5	0.11 ± 0.03	0.51	0.34 ± 0.10
10	AELA 885 (Manitoba)	1.3 ± 0.1	6.0	0.27 ± 0.03	1.2	0.20 ± 0.02
11	ELA 661 (Ontario)	7.3 ± 0.4	34	1.5 ± 0.1	7.0	0.20 ± 0.02
12a	ELA 241 surface (Ontario)	4.6 ± 0.3	21	1.3 ± 0.1	6.0	0.28 ± 0.03
12b	ELA 241 9 m (Ontario)					
12c	ELA 241 11 m (Ontario)	≥42 ± 1	≥193	≤ 5.9 ± 0.4	≤27	≤ 0.14 ± 0.02
13	Little Manito (Saskatchewan)	8.2 ± 0.5	38	0.69 ± 0.03	3.2	0.08 ± 0.01

Preliminary results from speciation studies show that high concentrations of plutonium as nonionic species were present in lake samples 11 and 12a (low pH lakes) and in the saline lake 13 which has $\sim 10^5$ ppm of sulfate present. High concentrations as ionic species occur in more strongly reducing environments, i.e., samples 10 (AELA 885, eutrophic-alkaline) and 12c (below the chemocline in meromitic ELA 241). The further interpretation of the data in this report awaits the outcome of analyses in progress at this time.

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THE OXIDATION STATE OF PLUTONIUM IN THE IRISH SEA

D. M. Nelson and M. B. Lovett*

Several of the chemical parameters needed to understand the distribution and behavior of plutonium in the aquatic environment have not been fully investigated in the field. The present study addresses two of the more fundamental of these parameters: (1) the oxidation state(s) of the plutonium present in seawater and (2) the extent to which each oxidation state is associated with suspended particulate matter.

The importance of oxidation state in determining the environmental chemistry of plutonium has frequently been implied.[1-4] Analytical procedures to separate the oxidation states have been published[5,6] and applied to laboratory samples. Laboratory experiments have also used plutonium, in initially specified oxidation states, to test the stability,[7] biological availability,[8] and attachment to sediments[9] of various oxidation states. However, to our knowledge no information has been published regarding the actual oxidation state(s) of plutonium found in natural waters.

The British Nuclear Fuels Ltd. reprocessing plant at Windscale, Cumbria, discharges plutonium into the Irish Sea via a submerged pipeline terminating 2.4 km offshore. This release supports plutonium concentrations of about 1 pCi/L in filtered seawater near the discharge,[10] and hence, this is an excellent experimental area in which to study the oxidation state(s).

Eight seawater samples were collected from the seven locations marked on Figure 1 during the summer of 1977. Shoreline samples were collected from water depths of about 0.5 m; offshore samples were collected either within 1 m of the surface or within 1 m of the seabed.

For each sample, the association of different oxidation states of plutonium with suspended particles was determined by measuring the concentration of each oxidation state in subsamples processes (1) without filtration, (2) after

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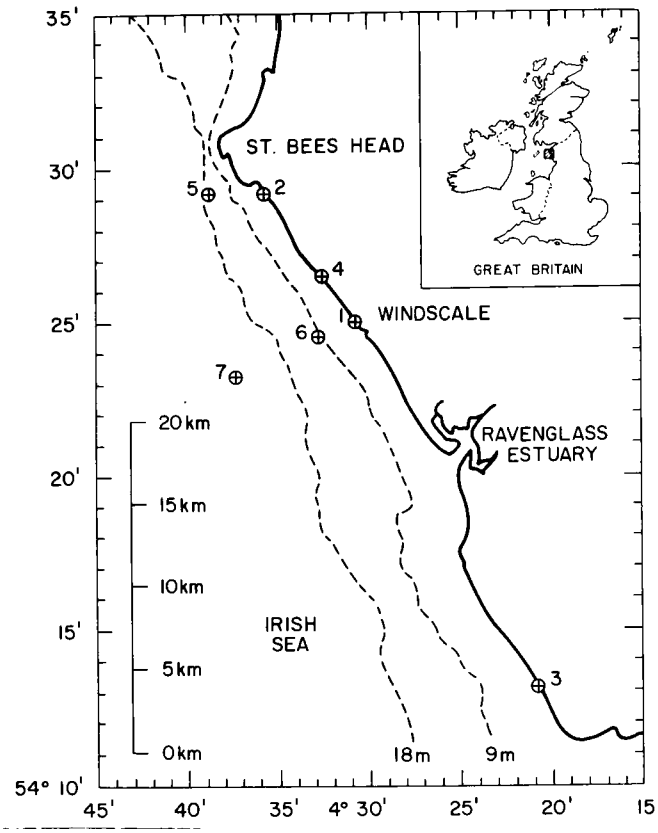

FIG. 1.--Location of water sampling stations in the Irish Sea near Windscale, United Kingdom.
(ANL Neg. 149-78-254)

filtration through an 0.22 μm membrane filter, and (3) after filtration through both 0.22 μm and 0.025 μm membrane filters. The method used for oxidation state differentiation was the classical separation of Pu(III) and Pu(IV) from Pu(VI) by the coprecipitation of the former pair on a rare earth fluoride.[11] Each subsample was made 0.8 M in HNO_2, 0.25 M in H_2SO_4, 0.5 mM in $K_2Cr_2O_7$, and 0.7 mM in $Nd(NO_3)_3$. Unfiltered subsamples stood overnight at this stage to allow exchangeable plutonium to leach from the particles before they too were filtered. Sufficient HF was added to raise the total fluoride concentration to 0.25 M, and the resultant NdF_3 precipitate was removed by filtration. Five grams of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2$ were added per liter of filtrate, which then stood overnight to complete the reduction of any Pu(VI) in the sample. NdF_3 was again precipitated by the addition of 100 mg of Nd per liter and removed by filtration. The plutonium in each NdF_3 precipitate was purified by routine techniques of anion-exchange,[12] and individual plutonium isotopes were determined by alphaspectrometry using silicon surface barrier detectors.

Completeness of the oxidation state separation and chemical yields were determined from the recovery of two isotopic diluents, ^{236}Pu(VI) and ^{242}Pu(IV),

added to each subsample as soon as possible after collection (or after filtration for filtered subsamples). Each tracer was isotopically pure and contained greater than 99% of its plutonium in the specified oxidation state. Overall chemical yields exceeded 80%, and oxidation state separations exceeded 97%.

Any Pu(III) initially present would accompany Pu(IV) through the analyses; any Pu(V) would be oxidized by the $Cr_2O_7^=$ and would, therefore, be included with the original Pu(VI). In a well oxygenated high pH system, such as surface seawater, the higher oxidation states in both the Pu(III):Pu(IV) and Pu(V):Pu(VI) couples were assumed to be the more likely, and subsequent results are reported as Pu(IV) and Pu(VI).

The Pu(IV) and Pu(VI) concentrations, tabulated by particle size class in Table 1, were calculated for each sample using the plutonium concentrations measured in the subsamples. These results indicate that plutonium retained on the filters is predominantly Pu(IV) and that plutonium passed in the filtrate is mainly Pu(VI). The simple act of filtering these samples provided a fair separation of the oxidation states; a feature which could prove useful in estimating the oxidation state present in previous measurements. Little plutonium of either oxidation state is removed by the 0.025 μm filter, suggesting that the plutonium which passes a 0.22 μm filter may be in true solution and not simply attached to very small particles. Furthermore, the ratio of Pu(VI) to Pu(IV) in solution, particularly for the offshore surface samples, is sufficiently constant to suggest that (1) the two are at or near oxidation-reduction equilibrium, or (2) the rate constants governing the approach to this equilibrium are slow compared with the initial rate of dispersion of Windscale effluent in the sea.

Assuming that there are heterogeneous exchange reactions for both Pu(IV) and Pu(VI) between seawater and suspended particulates, distribution coefficients (K_d = pCi · kg^{-1} in particles/pCi · L^{-1} in water) for each oxidation state as well as for total plutonium were calculated. These K_d values for each sample are given in Table 2. As the composition of suspended particulates is extremely variable, it is not surprising that the K_d's are far from constant. However, the general trends are unmistakable. While the K_d's measured for total plutonium are typical of values previously reported for the Irish Sea[10]

Table 1. Pu(IV) and Pu(VI) concentrations in water and suspended particulates.

Sample location	Type	Particle size[a]	^{239}Pu(IV),[b] fCi/L	^{239}Pu(VI), fCi/L	Pu(VI)/Pu(IV)
1	shoreline[c]	>0.22	6,200 ± 300	600 ± 200	0.096 ± 0.032
		<0.22	300 ± 40	1,250 ± 60	4.2 ± 0.6
2	shoreline[c]	>0.22	15,600 ± 500	610 ± 90	0.039 ± 0.006
		<0.22	70 ± 10	400 ± 30	5.7 ± 0.9
3	shoreline[c]	>0.22	8,400 ± 600	280 ± 90	0.033 ± 0.011
		<0.22	60 ± 10	220 ± 30	3.7 ± 0.8
4	shoreline[d]	>0.22	15,900 ± 900	200 ± 70	0.013 ± 0.004
		0.025—0.22	8 ± 4	54 ± 28	---
		<0.025	66 ± 3	791 ± 20	12.0 ± 0.6
5	surface[d]	>0.22	111 ± 8	7 ± 14	0.063 ± 0.126
		0.025—0.22	1 ± 4	-8 ± 13	---
		<0.025	33 ± 3	242 ± 10	7.3 ± 0.7
5	bottom[d]	>0.22	1,250 ± 52	28 ± 17	0.022 ± 0.014
		0.025—0.22	-1 ± 6	-10 ± 8	---
		<0.025	83 ± 4	200 ± 6	2.4 ± 0.1
6	surface[d]	>0.22	524 ± 19	-22 ± 18	-0.042 ± 0.034
		0.025—0.22	78 ± 8	34 ± 19	---
		<0.025	49 ± 3	399 ± 13	8.1 ± 0.6
7	surface[d]	>0.22	57 ± 7	22 ± 42	0.39 ± 0.74
		0.025—0.22	5 ± 4	42 ± 18	---
		<0.025	54 ± 3	443 ± 13	8.2 ± 0.5

[a] As defined by filtration through Millipore filters; this gives only a general indication of particle size.

[b] Total of ^{239}Pu + ^{240}Pu; ± 1 standard deviation counting error.

[c] Samples collected 21 June 1977; subsample size = 0.8 l.

[d] Samples collected 19 August 1977; subsample size = 4.0 l.

Table 2. Values of the distribution coefficient (K_d $L \cdot kg^{-1}$) calculated for Pu(IV) and Pu(VI).

Sample	Suspended load, mg/L	$^{239}Pu(IV)$,[a] $K_d \times 10^{-5}$	$^{239}Pu(VI)$, $K_d \times 10^{-5}$	^{239}Pu (total), $K_d \times 10^{-5}$
1	60	3.4 ± 0.5	0.08 ± 0.03	0.73 ± 0.05
2	110	20 ± 3	0.14 ± 0.02	3.1 ± 0.2
3	140	10 ± 2	0.09 ± 0.03	2.2 ± 0.3
4	40	60 ± 4	0.06 ± 0.02	4.7 ± 0.3
5S	2	17 ± 2	0.14 ± 0.29	2.1 ± 0.3
5B	5	30 ± 2	0.28 ± 0.17	9.0 ± 0.4
6	2	54 ± 4	-0.28 ± 0.23	5.6 ± 0.3
7	2	5.2 ± 0.1	0.25 ± 0.47	0.8 ± 0.4

[a] Total of ^{239}Pu + ^{240}Pu ± 1 standard deviation counting error.

and other systems[13] in these samples, the K_d's for Pu(IV) exceed those of Pu(VI) by factors of up to 1000. This is consistent with the behavior of thorium (IV) and uranium(VI) which are close chemical analogs for Pu(VI) and Pu(VI), respectively.

Because of this large difference in K_d, the initial distribution of plutonium between soluble and particulate phases in the sea should be highly dependent upon the ratio of oxidation states in the source material. Measurements of these ratios in Windscale effluent as well as at various distances from Windscale (and by inference at various times after release) are in progress. It is clear that a knowledge of the changes in oxidation state undergone by plutonium will be important in understanding the ultimate fate of this element in the environment.

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DISTRIBUTION OF CESIUM-137 IN LAKE ERIE

D. N. Edgington and J. O. Karttunen

Previous studies have shown that many radionuclides or trace elements, when introduced into the aquatic or marine environments, become rapidly associated with particulate matter and are deposited with the sediments.[1,2] Measurements of ^{137}Cs, $^{239,240}Pu$, and ^{210}Pb in the sediments of Lake Michigan have provided considerable insight into the processes, such as rates of removal, sedimentation rates, bioturbation, and redistribution, which govern their long-term biological availability in the water column.[3] Lake Michigan, however, is only typical of upper Laurentian Great Lakes which are essentially closed basins, and consequently there is no significant loss of introduced pollutants other than by transfer to the sediments. The lower Great Lakes are characterized by a short water residence time in the basin, and therefore, a considerable loss of added pollutants other than by transfer to the sediments.

Lake Erie provides a unique opportunity to study the influence of many limnological factors on the long-term retention of radioactivity in a lake basin because of the short residence time of water in the basin ($\sim$ 2.4 yr), the large surface to volume ratio, and the possibility of wind driven currents affecting the bottom of all but a small area of the eastern basin. Lake Erie consists of three distinct basins; the western basin, which is very shallow (< 20 m), receiving water from Lake Huron via Lake St. Clair and the Detroit River; the central basin, which is a little deeper (40 m); and the eastern basin, which has a small steep-sided deep basin (85 m). The characteristics of the surficial sediments have been described by Thomas et al.,[4] and the sources of the sediment have been documented by Kemp et al.[5]

On the basis of the known distribution of sediments in Lake Erie, a comprehensive sampling cruise was planned and executed in 1976. Sediment cores were retrieved from 36 stations representative of all areas of Lake Erie. These cores were sectioned on shipboard and immediately frozen in polyethylene bottles for storage. Measurements of ^{137}Cs were made using gamma-ray

spectrometry on the dried sample, and, knowing the fraction dry weight in each core, the total ^{137}Cs per unit area was determined for each core.

The distribution of ^{137}Cs in Lake Erie is shown in Figure 1. The contours drawn were based on the total ^{137}Cs found in each core, and a knowledge of distribution sediment type and thickness in the lake.[4] Integration over the whole area of the lake yields a total of 1530 Ci of ^{137}Cs in the sediments of the lake. An estimate of the total ^{137}Cs deposited directly into the lake as a result of wet and dry deposition may be made from the data for ^{90}Sr in rainfall accumulated over the last 25 years by HASL.[6] Since the closest monitoring station to Lake Erie is Wooster, Ohio, and the data reported from there are not significantly different from those used previously for a source term for Lake Michigan (from Argonne, Illinois, and Green Bay, Wisconsin) the same value will be used for this lake. The total deposition of ^{137}Cs (corrected for decay in 1976) has been 7.9 pCi $\cdot$ cm^{-2}, or 2010 Ci for the whole of Lake Erie. Therefore, the sediments of Lake Erie have retained 75% of the total ^{137}Cs delivered directly to its surface.

In addition Wahlgren has measured the concentration of ^{137}Cs in Lake Erie in the early summers (June) of 1973 and 1976. The values ranged between 11 and 25 fCi/L (average 19 ± 6) in 1973, and between 10 and 17 fCi/L

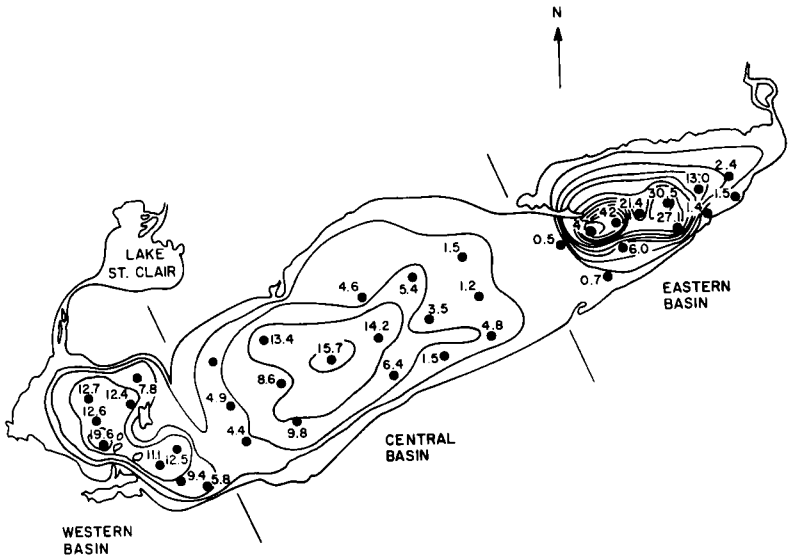

FIG. 1.--Distribution of ^{137}Cs in the sediments of Lake Erie expressed as pCi $\cdot$ cm^{-2}. Isopleths are shown for 1, 5, 10, 15, 20, 25, 30, 35, 40, 45 pCi$\cdot cm^{-2}$. Values for the individual cores are also given.
(ANL Neg. 149-78-253)

(average 14 ± 3) in 1976.* If the annual flux of ^{137}Cs to the surface of the lake is $\phi(t)$pCi/cm^2, the residence time of water in the lake is T_R years (volume of lake/outflow rate), and the residence time of ^{137}Cs in the water column is $T_{R'}$ years, then the concentration of ^{137}Cs in the water column as a function of time, C_L, is given by

$$\frac{dC_L}{dt} = \frac{A}{V}\Phi - \left(\lambda + \frac{1}{T_R} + \frac{1}{T_{R'}}\right) C_L = \frac{A}{V}\Phi - (\lambda + \gamma)C_L$$

or

$$C_L(t) = \frac{A}{V}\int_0^t \Phi(t')e^{-(\lambda+\gamma)(t-t')}dt' \quad , \tag{1}$$

where A is the area and V is the volume of the lake, λ is the radioactive constant, and $\gamma = \frac{1}{T_R} + \frac{1}{T_R}$. The loading to the sediments is given by

$$P_S = A \cdot \frac{T_R}{T_R + T_{R'}} \cdot \int_0^t \Phi(t')\left(1 - e^{-(\lambda+\gamma)(t-t')}\right)e^{-\lambda(t-t')} \cdot dt' \; . \tag{2}$$

Equations 1 and 2 provide two independent methods of evaluating $T_{R'}$ since T_R is known, C_L can be measured, and P_S can be calculated from the distribution of radioactivity in the sediments. Two assumptions made in this simple model are: (1) inputs of ^{137}Cs from the Detroit and other rivers are small; and (2) the water column of Lake Erie is well mixed both vertically and horizontally.

Since T_R is known, Eqs. 1 and 2 may be solved for $T_{R'}$. The resulting values of T_R, giving the best fit to the experimental data, are 1.05 yr for the water column and 0.80 yr for the sediments. The calculated values are compared in Table 1, and it is clear that the residence time of ^{137}Cs in the water column is about 1 year which is in agreement with independent estimates from the shape of the ^{137}Cs profiles in sediments from Lake Michigan.[7] These results indicate that it is possible to use a very simple model to calculate the distribution of a

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* We thank M. A. Wahlgren for making the results of these analyses available to us.

Table 1. Comparison of results using time-concentration model for ^{137}Cs in Lake Erie with actual observations. $T_R = 2.4$ yr

T_R, yr	Concentration in lake water, fCi/L				Total in sediments, Ci	
	1973		1976		1976	
	calc	obs	calc	obs	calc	obs
0.8	13.4	19 ± 6	9.7	14 ± 3	1530	1530
1.05	19.3		14.0		1430	

trace contaminants such as ^{137}Cs in a lake over relatively long periods of time provided that a reasonably accurate estimate of the inputs is known.

Finally, the total ^{137}Cs found in each basin can be compared to that which would be expected to be there on the basis of this model and the relative areas of each basin. If there is no redistribution of sediment among basins, the deposition should be proportional to the area of each basin. The distribution is shown in Table 2. There appears to have been no loss or gain of ^{137}Cs in the western basin, while approximately 250 Ci has been transferred from the central to the eastern basin.

These results are somewhat surprising, as the western basin is very shallow. The sediments are easily disturbed by wind-driven waves or vessels passing through, and considerable loss of ^{137}Cs would be expected due to resuspension and horizontal transport of the sediment. The retention of ^{137}Cs in the western basin may be due to factors such as a continuing supply of ^{137}Cs from Lake St. Clair and the Detroit River, and a circulation pattern essentially cut off from the remainder of the lake. Recently Thomas et al. have shown that a pollutant like mercury is not retained in the sediments of Lake St. Clair and is carried in the suspended particle load of the Detroit River to the western basin of Lake Erie.[8] Maps of surface and bottom currents of Lake Erie indicate that there may be a closed circulation pattern, at least in the summer months, in the western basin. The results of the ^{137}Cs distribution in the central and eastern basins add credence to the suggestion of massive redistribution of

Table 2. Distribution of ^{137}Cs in Lake Erie.

	Western basin	Central basin	Eastern basin	Whole basin
Area, km^2	5000	14800	6200	26000
Fractional area, %	19	57	24	100
Total measured ^{137}Cs, Ci	303	636	594	1533
Fraction in each basin, %	20	41	39	100
Calculated ^{137}Cs content, Ci [a]	300	880	370	1550
Net loss (-) or gain (+), Ci	0	-124	+230	0
Total deposition, Ci	-	-	-	2050

[a] see text.

sediments in large lakes that has been made by Edgington and Robbins on the basis of the study of the distribution of ^{137}Cs and ^{239}Pu in Lake Michigan sediments.[3] The ^{137}Cs profiles in cores from the central and eastern basins are indicative of similar remobilization of old sediment in that the concentration of ^{137}Cs in the upper few centimeters of the sediment column is far higher than would be expected from new inputs to the lake. In contrast, the ^{137}Cs profiles in the cores from the western basin indicate massive disruption and complete mixing down to about 8 cm.

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THE RELATIVE AVAILABILITY OF SELECTED TRACE ELEMENTS FROM COAL FLY ASH AND LAKE MICHIGAN SEDIMENT*

J. J. Alberts, † J. Burger, ‡ S. Kalhorn, ** C. Seils, and T. Tisue

The concentration of > 1 μm coal fly ash particles in Lake Michigan surface waters was found to be 10^5 to 10^6 per liter. With an expected residence time of one year, this concentration implies a flux to the sediment of 10^6 to 10^7 particles/cm^2/yr, or about 10^{-6} to 10^{-5} g/cm^2/yr. These calculations suggest that fly ash is currently a recognizable but quantitatively insignificant component of Lake Michigan sediment. A method is reported which uses a solid iminodiacetate chelating resin as the chemical analog of natural biological acceptors to simulate leaching at high dilutions in natural media. The availability of several trace elements from coal fly ash was compared by this technique to their availability from Lake Michigan sediment. Mn, Pb, and Zn, but not Fe, were released more readily from natural lake sediment than from fly ash. Therefore, fly ash appears not to contribute significantly to present fluxes of these elements to the lake.

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CHARACTERIZATION OF THE CHEMICAL ENVIRONMENT IN THE INTERSTITIAL WATER OF LAKE MICHIGAN SEDIMENTS

G. T. Tisue and D. N. Edgington

The chemical environment in sediment interstitial fluids is an important object of study for several reasons. Pore water chemistry reflects the course and rates of early diagenetic reactions.[1] Since many of the dissolved constituents are nutrients and/or metabolites, observations of their concentrations as a function of depth aid in establishing zones of activity for major classes of benthic microbes, such as sulfate reducing[2] or methanogenic bacteria.[3] The mineralization of organic matter of both natural and anthropogenic origin in turn depends on the presence of microbiological metabolic activity.[4] As the redox potential decreases with depth, some transition metal ions (e.g., Fe, Mn) are subject to changes in oxidation state that lead to increased solubility.[5] Ligands absent in the surface layers may appear at depth; $S^{=}$ produced during sulfate reduction is an important example. These changes in the chemical environment may affect the solubility of trace metals, thus influencing the rate at which and/or the extent to which sedimentation acts to remove potentially harmful constituents permanently from the lake.

We have designed and tested a sampling device to study the interstitial water chemistry of sediments. This device extracts the interstitial water from sectioned sediments without exposing the sediment to air. The details of the construction and operation of this apparatus will be the subject of a forthcoming communication. This report summarizes results of initial experiments and establishes the feasibility of the techniques in studies of broader scope.

Briefly, the sampling device permits a sediment core to be recovered, sectioned at 0.2 to 2.0 cm intervals, and squeezed to express and filter the interstitial fluid, while maintaining an inert atmosphere and temperatures near in situ values. Prompt and simultaneous electrochemical measurements may be made for as many as five constituents or properties on less than 20 mL of sample. Materials of construction and design of the sampling device were chosen to minimize contamination by metals. Thus, sensitive analyses may

be carried out subsequently in the laboratory for ultratrace constituents, including heavy metals.

With the cooperation of the Canada Centre for Inland Waters (CCIW), we were able to compare the operation of this interstitial water sampling device with the CCIW in situ sampler. The CCIW device follows the design proposed by Mangelsdorf et al.,[6] which permits sampling of the interstitial water without retrieving a sediment core. Figure 1 compares the results obtained by the two methods for soluble reactive silicate in the interstitial water of a Lake Ontario sediment core. The close agreement between the results obtained by these two methods indicates that our coring, sectioning, and squeezing operations do not seriously disturb the sediment profiles.

Figure 2 shows some of the properties of interstitial water from sediment cores taken in the southern basin of Lake Michigan about 12 km SW of Grand Haven, Michigan. The mineralogy and grain size distribution of sediment at this station were reported earlier,[7] as were estimates of the sedimentation rate by various methods.[8] The sediment surface consists of a layer of brown flock. About 1 or 2 cm beneath the interface there is an abrupt transition to a gray sandy silt, which is essentially featureless except for occasional black flecks. The uppermost 1 to 2 cm are disturbed by mysids, Pontoporeia, and small worms.

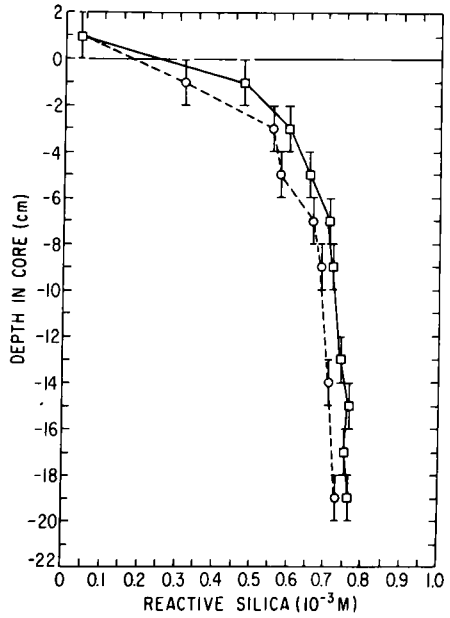

FIG. 1.--Reactive silica in Lake Ontario (Station 2, 1975) sediment pore fluids samples by two different methods. □ ANL squeezer; O CCIW in situ samples. (ANL Neg. 149-78-256)

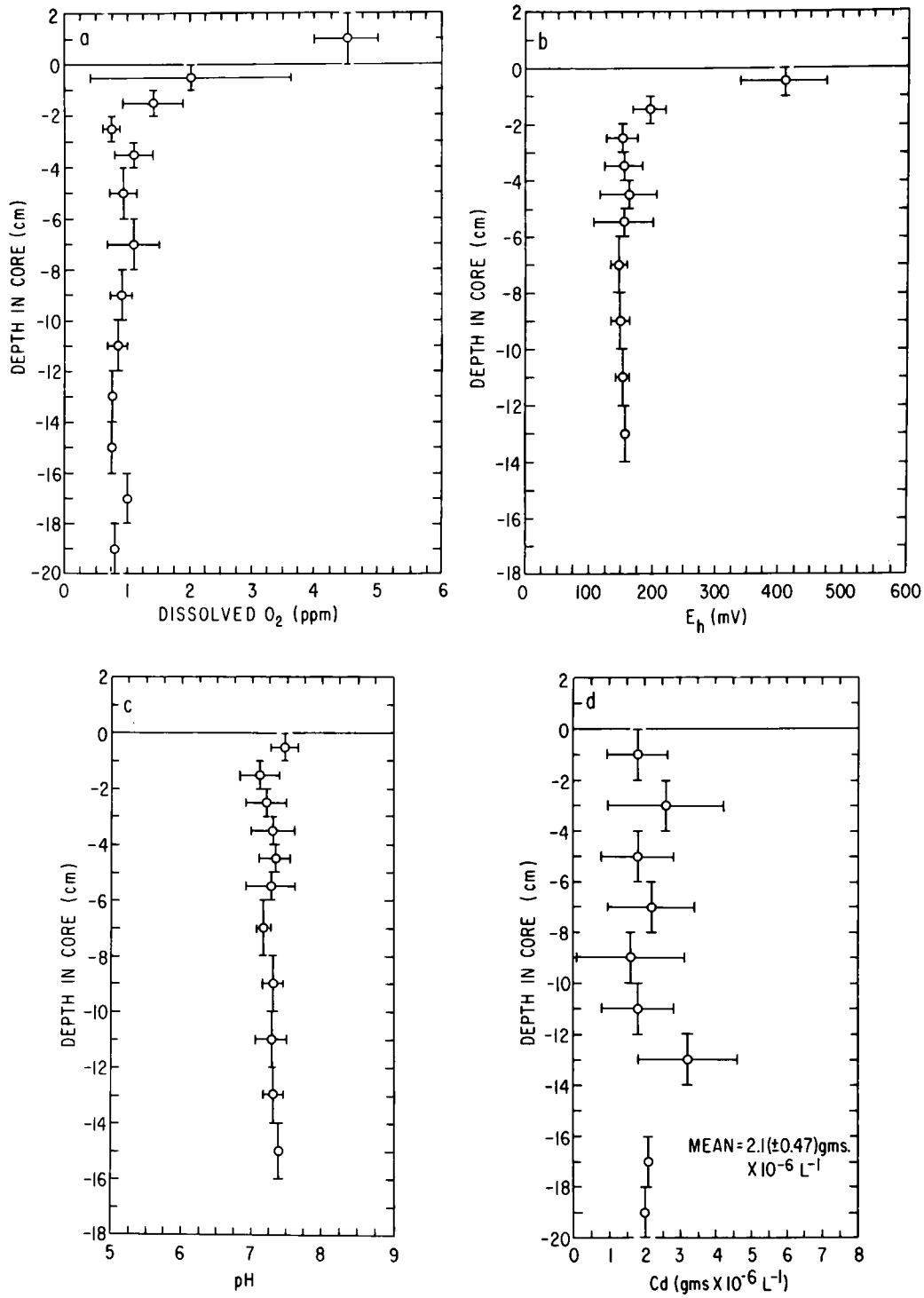

FIG. 2.--Properties of interstitial water from sediment cores taken at Station 5. Dissolved oxygen, 5 cores (a); redox potential, 5 cores (b), pH, 5 cores (c); and cadmium, 3 cores (d). (ANL Neg. 149-78-258)

Figure 2a shows the apparent persistence of small amounts of dissolved oxygen at depths up to 20 cm. We believe this puzzling observation is due neither to contamination by atmospheric O_2 nor to species which interfere with or poison the polarographic oxygen sensor. However, owing to well-documented shortcomings of this technique for determining dissolved oxygen,[9] we are seeking confirmation through other means of detection.

The Pt redox electrode measurements (Figure 2b) also indicate that conditions do not become strongly reducing in the upper 20 cm of the core. The pH values (Figure 2c) show little variation with depth, an observation that is also consistent with the maintenance of oxic conditions in this zone.

Attempts to determine sulfide using an ion-selective electrode failed to reveal detectable quantities of this species. Since the electrode gave a Nernstian response in synthetic standards down to a sulfide concentration of 10^{-7} M, the concentration in the interstitial water must be lower. It follows that little or no sulfate reduction to free sulfide occurs in the upper 20 cm, a hypothesis we are now testing by direct measurements for changes in sulfate concentration.

If sulfide is absent or produced very slowly, one might expect that the concentration of metals, such as Cd, Zn, and Pb, in interstitial water would be governed by the solubility of their carbonates rather than their much less soluble sulfides. The measured concentration of cadmium in interstitial water $\sim 2.1\ \mu g\ L^{-1}$ (i.e., $\sim 2 \times 10^{-8}$ M) is many orders of magnitude greater than the solubility of CdS would permit (Figure 2d) (if the concentration of $[S^{=}]$ is $\geq 10^{-7}$ M, $[Cd^{++}] \leq 10^{-24}$ M). On the other hand, since a fraction of the sediment material is calcite and/or dolomite, the interstitial water is likely to be saturated with calcium carbonate. If it is assumed that the sediments are a closed system and that the total carbonate concentration in the interstitial water is equal to that in the lake water, (10^{-3} M), then at pH 7.3, $[CO_3^{=}] = 1 \times 10^{-6}$ M. Thus, if the cadmium concentration in the interstitial water is governed by the solubility of $CdCO_3$, $K_{S_0} = 4 \times 10^{-14}$, the concentration of cadmium should be $4 \times 10^{-14}/10^{-6} = 4 \times 10^{-8}$ M. Considering the assumptions, the agreement between the measured and calculated values of $[Cd^{++}]$ is remarkable

and suggests that the cadmium in the interstitial water is in equilibrium with $CdCO_3$ in the sediments, and understaurated in the water column. Under these circumstances the sediments may act as a source of Cd to the overlying water (where the Cd concentration may be lower by two orders of magnitude).[10]

Acknowledgements

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DETERMINATION OF ULTRATRACE METALS IN LAKE MICHIGAN AND ITS TRIBUTARIES BY X-RAY FLUORESCENCE SPECTROMETRY

G. T. Tisue, C. Seils, and D. Bales*

Neither the tributary inputs nor the lakewide concentrations of trace metals are well characterized for Lake Michigan. There exists no baseline to which future changes in these constituents may be related. The multiplicity and low concentrations of important elements (typically < 10 ppb) create analytical problems, while the geographic extent of the lake, the large number of tributaries, and the risk of contamination, create sampling problems. Together, these factors dictate sampling and analysis schemes that are rapid, economical, sensitive, and applicable to many elements.

Energy dispersive x-ray fluorescence spectrometry recommends itself as a method for trace element analyses by virtue of its relative speed, economy, ease of sample preparation, and multi-element capability. But to realize these advantages, elements occurring at levels below about 0.2 ppm (10^{-3} g L^{-1}) must be concentrated prior to analysis. We are investigating these preconcentration techniques: precipitation with ammonium pyrrolidine dithiocarbamate (APDC),[1,2] adsorption on activated carbon, and chelation by selective reagents immobilized on controlled pore glass.[3] The analytical device being used in these studies was designed and built by members of this division.[4]

During the summer of 1977, we obtained samples from all the major river tributaries to the lake, as well as from nearshore surface waters at ten locations distributed along the entire shoreline. Particulate matter was removed at the time of collection by filtration through membrane filters. The unique pressure filtration apparatus used for this purpose permits rapid filtration of 10-L samples by applying N_2 pressures up to 50 psig. The material retained by the membrane filters is also being analyzed by energy dispersive x-ray fluorescence spectrometry in order to determine distribution coefficients

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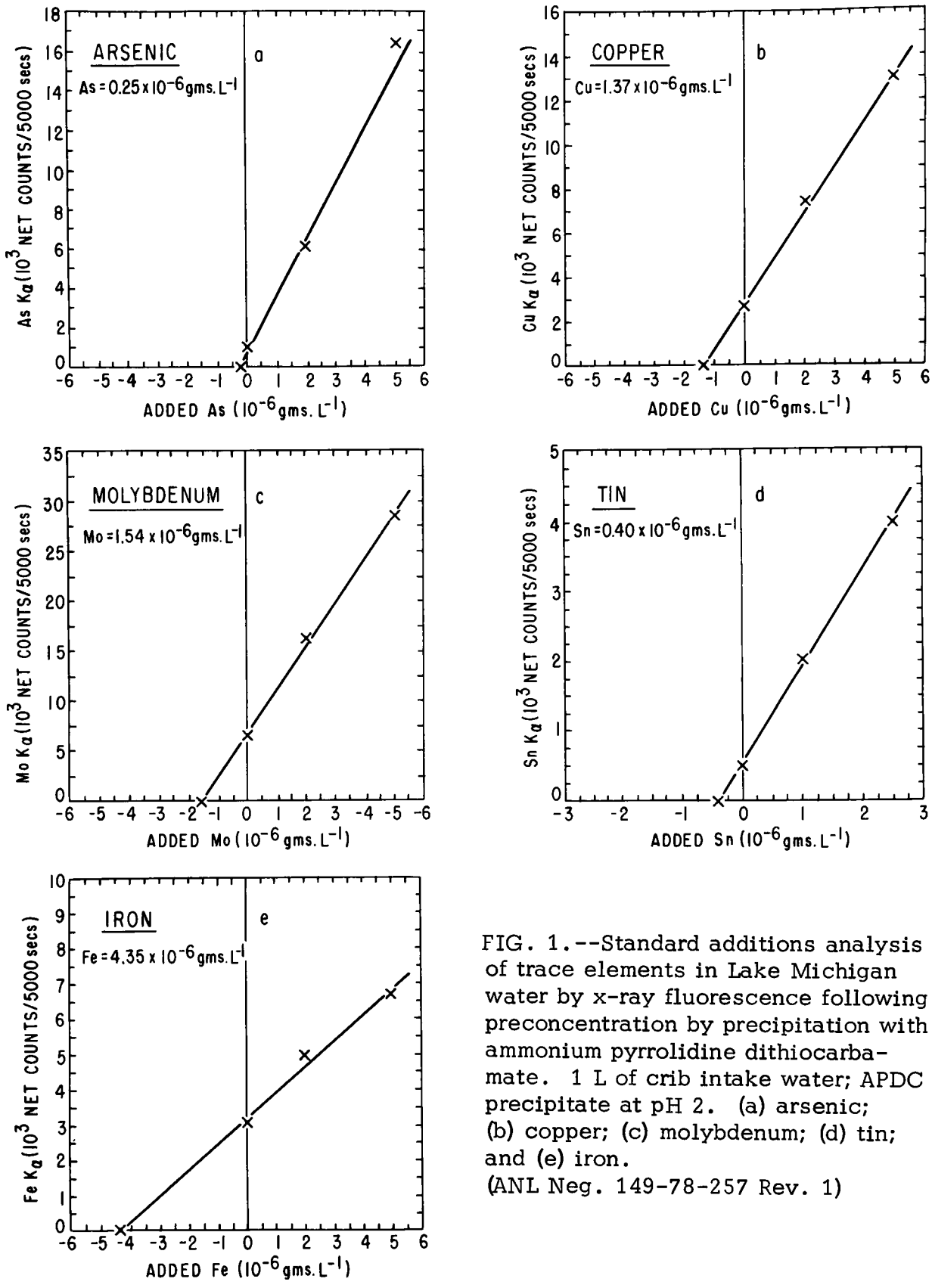

FIG. 1.--Standard additions analysis of trace elements in Lake Michigan water by x-ray fluorescence following preconcentration by precipitation with ammonium pyrrolidine dithiocarbamate. 1 L of crib intake water; APDC precipitate at pH 2. (a) arsenic; (b) copper; (c) molybdenum; (d) tin; and (e) iron.
(ANL Neg. 149-78-257 Rev. 1)

of trace metals between the particulate and dissolved phases. Figure 1 demonstrates the applicability of APDC preconcentration to determination of Fe, Cu, As, Mo, and Sn at the levels they occur in the lake. The 3-σ limits of detection were found to lie below 100×10^{-9} g L^{-1} for these five elements. Pb, Ni, Se, and perhaps Zn, are also detectable by this method.

To convert raw x-ray fluorescence spectral data to element concentrations requires background subtraction and deconvolution of overlapping peaks. Figure 2 shows the results of applying a "second derivative digital filter"[5] to the spectrum (upper trace) obtained from APDC metal complexes precipitated from the Muskegon River. The filtering technique effectively eliminates the slowly varying component due to backscattering while reducing overlap by giving more weight to those portions of a peak lying near the centroid. The data on which Figure 1 is based were processed in this fashion. These preliminary results encourage application of such preconcentration and data reduction techniques to the numerous samples we expect to obtain lakewide during the field season.

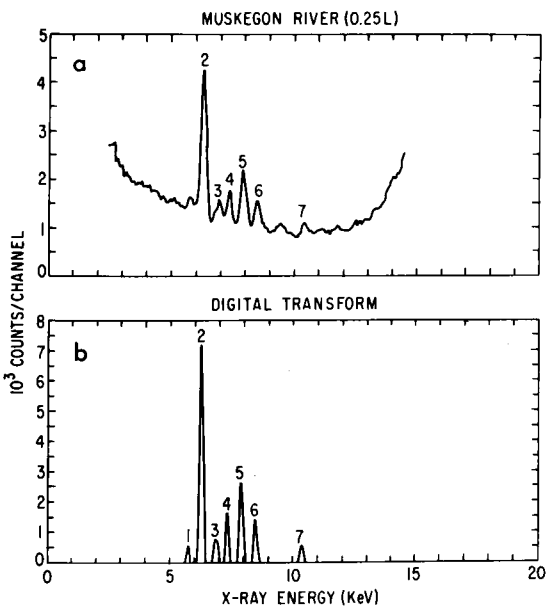

FIG. 2.--(a) Raw and (b) processed spectra of APDC precipitate from Muskegon River water showing the effects of the digital filtering technique on spectrum background and peak shape. 1, Mn in blank; 2, Fe 8.8 μg L^{-1}; 3, Fe (K_β); 4, Ni 2.4 μg L^{-1}; 5, Cu 2.8 μg L^{-1}; 6, Zn 0.8 μg L^{-1}; 7, As 0.2 μg L^{-1}; also present Mo and Sn.

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ACIDITY IN RAINFALL: ANALYSES AND SIMULATIONS*

G. Thomas Tisue and John Kacoyannikis**

Rainwater collected during nine precipitation events at Argonne National Laboratory has been analyzed for pH, acid and base neutralizing properties, and for nitrate, chloride, sulfate, and calcium (II). The results have been interpreted using a chemical model of acidity in rain based on straightforward ionic equilibria calculations. Comparison of the behavior predicted by this model and that observed when rainwater was titrated with strong acid or strong base confirms that rain may be treated as a solution of several strong acids, near equilibrium with atmospheric CO_2, that has undergone partial neutralization by bases such as NH_3. The results do not indicate the presence of significant amounts of acids having $pK_a < 7$, other than dissolved CO_2. Weak acids neither buffered the rain samples towards further acidification, nor contributed significantly to their base neutralizing capacity in the environmentally significant region below pH 5.5.

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